

# **Performance Report 2001/2002**

**Forschungsinstitut für Elektronenmikroskopie  
und Feinstrukturforschung  
Technische Universität Graz**

**Zentrum für Elektronenmikroskopie Graz**

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## Preface

This report contains an overview of the accomplishments of the Research Institute for Electron Microscopy (FELMI) of the Graz University of Technology during the period 2001 to 2002. In addition it includes the activities of the Center for Electron Microscopy Graz (ZFE Graz). The ZFE Graz is operated by the “Verein zur Förderung der Elektronenmikroskopie und Fein-strukturforschung” and works in close liaison with the FELMI.

The last two years were marked by the launch of new leading-edge instrumentation, like the purchase and installation of the first analytical high-resolution transmission electron microscope in Austria and of a new environmental scanning electron microscope. With this, the institute has made a huge leap forward, worthwhile to dedicate a section of this report to the present status and some future prospects of the department. We are very grateful to all our funding agencies for their continuous help and encouragement. The scientific part of the report will certainly provide sufficient evidence that all the money was well used.

In the final chapter we have furthermore included a few abstracts, which shall highlight the broad range of our collaborations with other university institutes and companies over the last two years.

During the last two years we could increase the number of presentations, scientific papers, co-operations with industry and support for PhD students. This was made possible by a significant growth of the number of collaborators to about 43 in December 2002.

Finally, the enthusiasm and the dedication of our collaborators at the institute should be honoured, being fundamental to our success. The key element for future progress of the institute continues to be their motivation to generate new ideas and to work hard.

A handwritten signature in black ink, appearing to read 'Ferdinand Hofer', with a long horizontal flourish extending to the right.

Ferdinand Hofer

February 2003



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# 1. The Institute: Present Situation and Future Prospects

## 1.1. Research Objectives

For both the development and application of advanced technology it is becoming increasingly important to characterize the structure of materials on the microscopic scale. Whether the interests are in diagnostic techniques for product development or applied materials research, understanding the microstructure and its relationship to the performance of the material is critical.

The FELMI of the TU Graz in co-operation with the ZFE Graz is one of the leading facilities in Europe for state-of-the-art atomic resolution characterization of materials. With several types of microscopes, it offers a comprehensive array of advanced imaging and spectroscopy techniques for studying technologically relevant materials and associated problems.

The institute attempts to take advantage from the synergies that emerge from the various fields of research interests, from different, sophisticated experimental tools and from fundamental research and applications of these techniques performed in conjunction with companies. Consequently, the FELMI-ZFE tries to improve existing microscopy preparation and characterization techniques and/or to develop new techniques especially in the field of materials science. At the same time it applies these techniques to the characterization of all kinds of materials, providing efficient answers and solutions to materials science problems.

During the last two years there have been co-operations with about 60 university institutes and 100 companies (mainly from Styria but also from Europe and overseas). During this period 29 graduate and 46 PhD students (mainly from the TU Graz) benefited from the support of the institute.

During the last decade several research groups have been established in the institute, each of them focussing on a specific aspect of microscopy or materials.

- Microanalysis using scanning electron microscopy and related techniques (P. Pölt)
- Transmission electron microscopy and specimen preparation (P. Warbichler)
- Analytical electron microscopy (F. Hofer)
- Microscopy of polymers and biological tissue (E. Ingolic)
- FTIR- and Raman microspectrometry (P. Wilhelm)
- Apparatus development (A. Aldrian)

In a meeting of the scientific and economical advisory board held on May 5<sup>th</sup>, 2000 this strategy has been esteemed worthwhile. Nevertheless, certain profound changes in the scientific environment have caused a reorganization and shift of our activities towards:

- Focus on nanostructured materials, development of new nanomaterials
- Emphasis and combination with theoretical approaches (simulation of EELS near edge fine structures and high resolution TEM images)
- Introduction of new innovative characterization methods.

## 1.2. Research Tools and New Developments

The research is based on sophisticated equipment operated by specialized groups. The goal is to develop group activities in the framework of already existing or new collaborations ensuring other institutes can benefit as well. On one hand research, spread out over several groups, favours the exchange of knowledge, of scientific results and improves the publicity of our work, but secondly reduces the total cost of ownership for instrumentation, which otherwise would be far too high for just one institute.

A significant portion of electron microscopes of the Graz University of Technology are kept in the institute. We have been successful in continuously upgrading the instrumentation but

also in educating our scientists and microscope operators better in order to provide state-of-the-art investigations both for university institutes and companies.

Our laboratory now includes one analytical high-resolution electron microscope, two analytical transmission electron microscopes, one environmental scanning electron microscope, several scanning electron microscopes as well as FTIR-, Raman and advanced light microscopy. Associated techniques include energy-dispersive x-ray analysis (EDX), wave length dispersive x-ray analysis, elemental mapping, electron energy-loss spectrometry, energy-filtering microscopy, low-dose imaging, electron diffraction and many other special techniques.

- **Analytical high resolution electron microscope (HR-AEM)**

The first analytical high resolution electron microscope in Austria was installed in the turn of 2000/2001. This microscope is equipped with a field emission gun, a high resolution objective lens, an energy-dispersive x-ray detector and an imaging filter. With the instrument we could improve the resolution of a variety of important characterization techniques such as HREM, EELS, EFTEM and STEM. Consequently it is used for characterizing materials at nearly atomic resolution, and it shall help to meet the challenges of new classes of materials and devices, like nanostructured materials, nanoparticles, semiconductor devices and functional materials.

In a second step we could extend the resolving power of the microscope by installing a high resolution energy-filter and a monochromator for the electron gun. Energy resolution can now be improved from about 0.6 eV to less than 0.2 eV which gives access to chemical bonding information in nanometer small specimen areas, harnessing the near edge-fine structures in EELS spectra. This will be especially helpful for studying inner boundaries in materials and single nanoparticles. The monochromated TEM is the second unit in the world besides the installation at TU Delft (The Netherlands). The extension was enabled by a special cooperation project with FEI (Eindhoven, The Netherlands) and Gatan (Pleasanton, USA), which was financially co-funded by the „Forschungsförderungsfonds der Gewerblichen Wirtschaft“ (FFF) in Vienna and by the „Steiermärkische Landesregierung“ in Graz.

The complete microscope investment amounted to a total of about 1,75 Mio Euro, which was raised by the TU Graz (25%) and by the „Verein zur Förderung der Elektronenmikroskopie und Feinstrukturforschung“ (75%) with the help of project grants.

- **Low-vacuum scanning electron microscope (Environmental SEM = ESEM)**

In the last year one outstanding event for our institute was the delivery of the low-vacuum scanning electron microscope which was installed during June 2002 and which will enable a broad range of new characterization techniques. The new microscope will be used for the studying of „wet“ samples at high spatial resolution and is equipped with a cooling and heating stage as well as a strain and tensile stage. In this outfit, the microscope is particularly suited for “in-situ” studies such as phase transitions, corrosion properties, high temperature behaviour, drying processes and so on. We plan to use it mainly for problem solving in the fields of technical chemistry, biochemistry, biology and biotechnology. The microscope was delivered by FEI (Eindhoven, The Netherlands) and will be upgraded with a field emission gun in April 2003.

In order to install the complete microscope including all necessary extensions we had to invest about 0.7 Mio Euro: The project was launched by the „Verein zur Förderung der Elektronenmikroskopie und Feinstrukturforschung“ with the support of the „Steirische Wirtschaftsförderung“ (SFG) in Graz and the „Wachstumsförderung“ of the Federal Ministry of Economics and Labour (BMWA) in Vienna. Part of it was supported by the TU Graz within a special project financed by the „Rat für Forschungs- und Technologieentwicklung“ (RFT) in Vienna.

- **„Focussed Ion Beam“ machine (FIB)**

From 2001 to 2002 we intensively strove for the purchase of an urgently needed FIB machine. Our constant efforts have been successful, because finally the „Rat für Forschungs- und Technologieentwicklung“ (RFT) in Vienna recommended our project. Consequently, the Federal Ministry for Education, Science and Culture in Vienna financed the FIB-machine. After a long testing period we decided to order a FIB-machine (DUALBEAM) from FEI (Eindhoven, The Netherlands) in October 2002. The instrument allows to cut and mill cross-sections of surfaces, defects and nanosized structures and to deposit nanostructures and thin films. In order to enable high resolution imaging a scanning electron microscope is included. The instrument is specifically tailored to the needs of our institute and will be delivered in June 2003.

### 1.3. Most significant scientific results

This chapter summarizes some of the most significant results obtained during the last period. Most of them have already been published in major scientific journals.

- Fundamental studies of the limits of spatial resolution of energy-filtering transmission electron microscopy (EFTEM) in co-operation with the National Center for Electron Microscopy (NCEM) at the LBNL in Berkeley (USA).
- HREELS of transition metal oxides (co-operation with Gatan Inc, USA; FEI, Eindhoven, NL; the Fritz-Haber-Institut in Berlin and the TU Delft, NL).
- Development of new data reduction techniques for EELS and EFTEM Spectrum Imaging such as „elemental occurrence maps“.
- Development of a new wet chemical technique for the preparation of metallic nanoparticles exhibiting previously unknown morphologies.
- Successful preparation of a new class of two component oxide nanoparticles using aerosol techniques, in co-operation with VTT, Espoo (Finland).
- Development of a novel EFTEM technique for imaging of nanometer thin oxide layers in silicon based semiconductor devices.
- Introduction of electron backscatter diffraction (EBSP) in the scanning electron microscope in the institute and first successful applications in co-operation with the „Institut für Werkstoffkunde und Schweißtechnik“ of the TU Graz.
- Development of a new method for the determination of orientation and crystallinity of polypropylene using micro-Raman spectrometry.
- Successful characterization of many newly developed materials, e.g. steels and alloys with nanosized precipitates, nanostructured coatings and nanoparticles, partly in co-operation with the Instituto de Ciencia de Materiales, Sevilla, Spain.

### 1.4. “The life” of the laboratory

During the last two years, the situation of the institute was difficult due to the enormous efforts to improve the instrumentation and to maintain the staff. However, the enthusiasm of the staff and broad support from outside allowed us to overcome many of the problems. Indeed, thanks to the broad diversity of contracts and partnerships, we could further increase the number of employees and PhD students.

#### Staff

Change of staff during the last two years has been considerable when compared with the years before. Due to several reasons we expect this situation to continue in the future.

- The vice head of the institute, Ass.-Prof. Dipl.-Ing. Dr.techn. Peter GOLOB, retired on February 28, 2001. Dr. Golob was heading the workgroup „Microanalysis and

Scanning Electron Microscopy“. He was member of the institute since 1968 and co-leader of the institute from January 1<sup>th</sup>, 1989 on.

- Ing. Hanns Waltinger retired on Juni 1<sup>st</sup>, 2001. Ing. Waltinger was heading the workgroup “Scanning Electron Microscopy” and has been a member of the institute since 1970.
- Daniela Rauchenwald left the institute (ZFE Graz) in January 2002.
- Ing. Adolf Aldrian retired on December 31, 2002. Ing. Aldrian was heading the workgroup „Apparatus development“ and he has been a member of the institute since 1960.
- Dr. Werner Grogger returned on March 1<sup>st</sup>, 2001 from a 1 ½ year sabbatical at the National Center for Electron Microscopy at the LBNL (Berkeley, USA) (Max-Kade scholarship).
- Sanja Simic entered of the institute on May 15<sup>th</sup>, 2001 (ZFE Graz) and is working in the group of Dr. Pölt.
- Margit Wallner started at the insitute on January 1<sup>st</sup>, 2002 (ZFE Graz) and is working in the photo laboratory group, led by DI Zedlacher).
- Christian Brandl is member of the institute since April 1<sup>st</sup>, 2002 („Teilrechtsfähigkeit“ of the FELMI) and is joining the group of Dr. Wilhelm.
- Manuel Paller started on July 1<sup>st</sup>, 2002 (ZFE Graz) and is working in the group of Dr. Warbichler.
- MMag. Werner Rechberger became member of the institute on June 1<sup>st</sup>, 2002 („Teilrechtsfähigkeit“ of the FELMI) and participates in the group of Dr. Hofer on nanoanalysis of steels and alloys.
- Dipl.-Ing. Bernhard Schaffer started on September 1<sup>st</sup>, 2002 (Special Research Programme „Elektroactive Materials“ and is working at the FELMI in the group of Dr. Hofer on the characterisation of electroactive materials.
- Dipl.-Ing. Michael Toth is member of the institute since October 1<sup>st</sup>, 2002 („Teilrechtsfähigkeit“ of the FELMI) and joins Dr. Hofer’s group on the development of nanostructures.
- Dipl.-Ing. Armin Zankel entered on November 1<sup>st</sup>, 2002 („Teilrechtsfähigkeit“ of the FELMI) and is working in the group of Dr. Pölt on in-situ studies with the new ESEM.
- Dr. Mario Schmied passed a course for quality management of the TÜV Austria.
- Dr. Ilse Papst passed a course for administration at the “Verwaltungsakademie” in Vienna.
- „Outstanding Poster Award“ for Dipl.-Ing. Andreas Gupper at the FACSS 2002 in Providence, USA.
- Dr. Mario Schmied got a special acknowledgement prize of the company ANTON PAAR for the achievements in his doctoral thesis which was presented in March 2002.

#### Most significant equipment bought in 2001-2002:

Due to the co-operation of the FELMI with the ZFE, the following equipment could be purchased:

- Analytical high resolution electron microscope: TECNAI F20 provided by FEI (Eindhoven) with a FEG, HR-STEM with HAADF-detector, energy dispersive x-ray spectrometer (EDXS), a high resolution imaging filter and a monochromator; financed by TU Graz, „Verein zur Förderung der Elektronenmikroskopie“ with the support of the „Forschungsförderungsfonds der Gewerblichen Wirtschaft“, Wien, „Steiermärkische Landesregierung“ in Graz and the „Wachstumsförderung“ of the Federal Ministry for Economics and Labour (BMWA), Vienna.
- High resolution scanning electron microscope (low-vacuum instrument with a FEG), equipped with an EDX-spectrometer, heating stage and strain- and tense stage; financed by the „Verein zur Förderung der Elektronenmikroskopie“ with the support of the „Steirische Wirtschaftsförderung“ (SFG) in Graz, the „Wachstumsförderung“ of the

Federal Ministry of Economics and Labour in Vienna and by the project, which has been passed by the “Rat für Forschungs- und Technologieentwicklung”, Vienna.

- FT-infrared microscope with special objectives (surface analysis with ATR, thin films with GIR), prepared for the upgrade with an imaging device (FPA imaging detector), supported with the project of the TU Graz, which has been passed by the “Rat für Forschungs- und Technologieentwicklung”, Vienna.
- CCD-camera from Gatan for the transmission electron microscope Philips EM420 (supported by the „Wachstumsförderung“ of the Federal Ministry of Economics and Labour, Vienna).
- Light microscope „3D Infinite Focus“ from ALICONA, Grambach for the automatic image acquisition and analysis of large specimen areas at high depth of view (ZFE Graz).
- Development of a low energy ion milling apparatus based on an instrument of the ZFE Graz with new ion guns from Technoorg Linda (Budapest) for the improvement of TEM-specimen preparation (ZFE Graz).
- Installation of an electrolytical thinning apparatus from Struers for TEM-specimen preparation (supported by the „Wachstumsförderung“ of the Federal Ministry of Economics and Labour, Vienna).

#### Acceptance in the scientific community

- F. Hofer is member of the editorial board of MICRON, board member of the Austrian Society for Electron Microscopy (ASEM) and co-chairman of the supervisory board of the company ANTON PAAR in Graz.
- F. Hofer was member of the international advisory board of the “Dreiländertagung für Elektronenmikroskopie” in Innsbruck, Austria (2001) and of the International Congress for Electron Microscopy (ICEM in Durban, South Africa (2002).
- G. Kothleitner is board member of the Working Group “EFTEM & EELS” within the German Electron Microscopy Society (DGE), since 2002.
- Staff members were active as referees both for scientific institutions and scientific journals: VolkswagenStiftung Hannover, BRD; Netherlands Organization for Scientific Research (NWO); Institut für Festkörper- und Werkstoffforschung, Dresden, BRD; University of Cambridge, U.K., University of Antwerp, Belgium. Ultramicroscopy, Microscopy & Microanalysis, Micron, J. Microscopy, J. Electron Microscopy, Mikrochimica Acta, Chemical Monthly, Chemistry of Materials, Spectrochimica Acta B, Philosophical Magazine A, Vacuum, Applied Physics Letters, Physical Review Letters, Macromolecular Symposia.
- International Symposium, organized at the TU Graz on June 12<sup>th</sup>, 2001 on the occasion of the 50<sup>th</sup> anniversary of the institute and the inauguration of the new high resolution electron microscope.
- Collaboration with research groups from the Styrian Universities in the Special Research Programme “Electroactive Materials” will continue until April 2006.
- The FELMI is actively engaged in establishing a new university course of the TU Graz for “Nanotechnology and Nanoanalysis”.
- Cooperation with competence centers such as the Materials Center Leoben and the ABC-Center at the TU Graz is extended.
- Cooperation with several European institutes within COST523 „Nanostructured materials“, spanning from Sevilla to Helsinki.
- The institute participated in the presentation of the TU Graz at the “Hannover Fair” in Hannover, Germany during March 2001.
- The institute successfully participated at the “Materialica” fair in Munich, Germany during September 2002; in co-operation with the “Steirische Wirtschaftsförderung” (SFG).

- The number of invited talks given by members of the institute abroad increased considerably and the activities were spread out ranging from America over Europe to Australia and China.
- ZFE Graz Wachstumsförderung is a member of the Austrian Cooperative Research (ACR) with several scientific cooperations with other ACR institutes.

#### The institute in the news

- *Kleine Zeitung*, 10. Juni 2001.  
„Eine Superlupe für Steirer“
- *ORF-TV-Report in „Steiermark Heute“*, 15. Juni 2001.
- *Jahresbericht 2000/01 TU Graz*  
„Seeing the Invisible: Mikroskopie mit atomarer Auflösung“
- *Kleine Zeitung*, 6. Jänner 2002  
„Bizarre Reise in die Tiefe“
- *Forschungsjournal der TU Graz WS 2001/02*  
„Seeing the Invisible“
- *VIA Airportjournal Graz 5/2002*  
“Graz sieht mehr: Mit dem ersten Hochauflösungselektronenmikroskop Österreichs”

### **1.5. Plans for the future**

A major point of focus is to fully exploit existing instrumentation and to introduce new leading edge instrumentation. Here we will focus on the following developments:

- Focal Plane array (FPA) detector for the new FT-IR microscope from Bruker.
- Focussed ion beam machine for electron microscopic specimen preparation; mainly for semiconductor devices and coatings on materials; delivery during June 2003.
- High resolution scanning electron microscope; planned for 2005.
- Atomic force microscope in a scanning electron microscope, planned for 2004.
- Replacement of out-dated equipment which is still under usage for routine work e.g. old EDX-spectrometer or computer facilities.
- Development of a business-plan for the ZFE Graz until June 2003.

Besides enforced co-operations with other institutes from other Styrian Universities in the planned special research project “Nanocomposites” we hope to increase scientific exchange through cooperation with well known research institutes throughout the world. To give an example, we are presently actively co-operating on the preparation of a “Network of Excellence” on transmission electron microscopy which is coordinated by Prof. Dr. Christian COLLIEX (Université Paris-Sud, France). This project will be submitted to the 6<sup>th</sup> Frame Programme of the European Union and the institute will coordinate the local node for Austria, Hungary and Slovenia. For the next years we also plan to bring scientific congresses and workshops to Styria: 2003 we will organize a workshop on the topic “EELS of STEELS” and 2005 we will host an international EELS-EFTEM workshop.

### **1.6. Acknowledgements**

The experimental work in a scientific institute in the field of high resolution microscopy not only needs full motivation of all collaborators, but also significant financial support. Without the help of many institutions it would not be possible to provide and to maintain this level of the instrumentation, the co-operations and the quality of the results presented in this performance report. We are especially grateful to the officials of our university, Rector O.Univ.-Prof.Dr. Erich HÖDL, the Vice-Rectors Hofrat Dr. Johann THEURL and O.Univ.-Prof. Dr. Hans SÜNKEL as well as the central administration of the university.

Financial support of our work was granted by many subsidizing organisations. These are in particular the „Forschungsförderungsfonds der Gewerblichen Wirtschaft“ (FFF) in Vienna, the „Forschungsförderungsfonds der wissenschaftlichen Forschung“ (FWF) in Vienna, the „Steirische Wirtschaftsförderung“ (SFG), the „Steiermärkische Landesregierung“ in Graz (Landesrat Dipl.-Ing. Leopold SCHÖGGL), Austrian Cooperative Research (ACR), the Federal Ministry of Economics and Labour (BMWA) in Vienna and our industry co-operation partners plus all institutions at home and abroad.

Last but not least we must particularly thank Prof. DI Helmut LIST, Komm.Rat DI Ulrich SANTNER and Komm.Rat DI Helmut KATZENBERGER, who spend much of their valuable time supporting our work in the “Verein zur Förderung der Elektronenmikroskopie”.

**Symposium:**

**“50 Years Electron Microscopy at the Graz University of Technology”** June 13<sup>th</sup>, 2001.



Prof. Christian Colliex  
(Université Paris-Sud,  
Orsay, France)



Prof. Manfred Rühle  
(Max-Planck-Institut f.  
Metallforschung, Stuttgart,  
BRD)



Presentation of the new analytical high resolution electron microscope (Tecnai F20)

The former heads of the institute:  
Ao.Univ.Prof. Hofrat Dr. Wolfgang Geymayer  
and  
Hofrat Dr. Fritz Grasenick  
(from left).



o.Univ.-Prof. Dr. Hans Sünkel  
Vice Rector of the TU Graz



Prof. DI Helmut List  
President of the „Verein zur  
Förderung der  
Elektronenmikroskopie“

# 1. Das Institut: Gegenwärtige Situation und zukünftige Entwicklung

## 1.1. Forschungsziele

Sowohl für die Entwicklung als auch für die Anwendung moderner Technologien wird es zunehmend bedeutsam, die Struktur von Festkörpern und funktionellen Bauelementen in mikroskopischen Bereichen zu charakterisieren. Die Interessensgebiete reichen von Diagnosen im Bereich der Produktentwicklung bis zur angewandten Materialforschung, wo die Kenntnis der Mikrostruktur und ihr Zusammenhang mit technologischen Eigenschaften von grundlegender Bedeutung ist.

Das Institut ist eine der führenden Einrichtungen Mitteleuropas im Hinblick auf die modernsten Verfahren der Mikrostrukturuntersuchung mit bis zu atomarer Auflösung sowie der Nanobereichsanalyse von Werkstoffen. Das breite Spektrum verschiedener mikroskopischer Untersuchungsmethoden ermöglicht umfassende Aussagen in bezug auf Morphologie, Kristallographie und chemischer Zusammensetzung und ist daher für technologische Problemlösungen ideal geeignet.

Die wissenschaftliche Ausrichtung des Institutes zieht Vorteile aus den Synergien zwischen den verschiedenen Forschungsrichtungen, zwischen verschiedenen sich ergänzenden, anspruchsvollen experimentellen Einrichtungen sowie zwischen Grundlagenforschung und Anwendung elektronenmikroskopischer Verfahren für Industrieforschung. Dementsprechend versuchen wir einerseits die bestehenden mikroskopischen Präparations- und Charakterisierungstechniken besonders im Bereich der Materialwissenschaften zu verbessern, andererseits wenden wir diese Techniken zur Charakterisierung aller Arten von Werkstoffen, Festkörpern und technischen Produkten an.

Während der letzten zwei Jahre kooperierten wir mit über 60 Universitätsinstituten und 100 Industriebetrieben, wobei sich diese Aktivitäten vorwiegend auf die Steiermark, einige aber auch Europa und Übersee erstreckten. In diesem Zeitraum wurden außerdem 46 Dissertationen und 29 Diplomarbeiten (hauptsächlich Studenten der TU Graz) in bezug auf elektronenmikroskopische Untersuchungen betreut.

Im Laufe des letzten Jahrzehnts haben sich Forschungsbereiche entwickelt, von denen sich jeder auf einen bestimmten Aspekt der Mikroskopie spezialisiert hat:

- Rasterelektronenmikroskopie und Mikrobereichsanalytik (P. Pölt)
- Transmissionselektronenmikroskopie und Probenpräparation (P. Warbichler)
- Analytische Transmissionselektronenmikroskopie (F. Hofer)
- Mikroskopie von Polymeren und biologischen Geweben (E. Ingolic)
- FTIR- und Raman-Mikrospektroskopie (P. Wilhelm)
- Geräteentwicklung (A. Aldrian)

Die Zielsetzungen des Institutes wurden anlässlich des Treffens seines Wissenschafts- und Wirtschaftsbeirates am 5. Mai 2000 als richtungsweisend beurteilt und sollen als Hauptkriterien für die Festlegung der Entwicklungsrichtungen beibehalten werden. Dennoch haben uns tiefgreifende Änderungen im wissenschaftlichen Umfeld bewogen, gewisse Schwerpunkte vorsichtig an aktuelle Entwicklungen anzupassen, die in den letzten beiden Jahren innerhalb der bereits bestehenden Arbeitsgruppen realisiert werden konnten:

- Verstärkte Fokussierung auf nanostrukturierte Materialien, u.a. Entwicklung von neuartigen Nanomaterialien
- Verstärkte Anwendung theoretischer Verfahren (Simulation von EELS-Nahkantenfeinstrukturen und Hochauflösungsbildern)
- Einführung neuer innovativer Charakterisierungsmethoden.

## 1.2. Instrumente und neue Entwicklungen

Für die Forschungsarbeiten des Institutes werden sehr anspruchsvolle Einrichtungen eingesetzt, die durch spezialisierte Arbeitsgruppen betrieben werden. Es ist unser Bestreben die Aktivitäten dieser Arbeitsgruppen im Rahmen bereits existierender oder neuer Kooperationen zu verstärken und die Zugänglichkeit für andere Institute sicherzustellen, da einerseits die Kosten derartiger Geräte für einzelne Institute zu hoch wären, und andererseits das Arbeiten in größeren Gruppierungen den wissenschaftlichen Austausch begünstigt und dies die Verbreitung unserer Ergebnisse verbessert.

Da das Institut eine zentrale Einrichtung der TU Graz darstellt, ist ein Großteil der Elektronenmikroskope unserer Universität im Institut konzentriert. Daher ist es auch unser Ziel die Instrumentierung ständig weiter zu verbessern sowie den Wissensstand unseres wissenschaftlichen Personals und der Bedienungsmannschaft voranzutreiben, sodass höchstwertige Untersuchungen sowohl für Universitätsinstitute als auch für die Industrie gewährleistet werden können.

Unser Institut umfasst derzeit drei analytische Transmissionselektronenmikroskope, mehrere Rasterelektronenmikroskope, ein FTIR- und ein Raman-Mikroskop-Spektrometer. Die ergänzenden Verfahren erstrecken sich auf Energie- und Wellenlängen-dispersive Röntgenspektrometrie, Elektronenenergieverlustanalyse, energiegefilterte und element-spezifische Abbildungen, Elektronenbeugung und andere spezielle Techniken.

- **Analytisches Hochauflösungselektronenmikroskop (HR-AEM).**

Zur Jahreswende 2000/2001 wurde das erste analytische Hochauflösungsmikroskop Österreichs installiert. Dieses Mikroskop ist mit einer Feldemissionskathode, einer Hochauflösungs-Objektivlinse, einem EDX-Spektrometer und einem abbildenden Energiefilter ausgerüstet. Mit diesem Mikroskop konnte das Auflösungsvermögen einer Reihe wichtiger Charakterisierungsverfahren, wie HREM, EELS, EFTEM, STEM entscheidend verbessert werden. Dieses neue Instrument wird für die Charakterisierung von Materialien bei atomarer Auflösung eingesetzt werden. Es soll helfen die Herausforderungen durch neue Klassen von Werkstoffen, z.B. nanostrukturierten Materialien, Nanoteilchen sowie Halbleitermaterialien und funktionellen Bauelementen, zu meistern.

In einem zweiten Schritt wurde dieses Mikroskop mit einem Hochauflösungs-Energiefilter und mit einem Monochromator für die Verbesserung der Energieauflösung in der Elektronenenergieverlustspektrometrie von vorher etwa 0,6 eV auf unter 0,2 eV ausgerüstet. Damit wird es erstmals möglich Aussagen über chemische Bindungsverhältnisse in Nanometer kleinen Probenbereichen z.B. in inneren Grenzflächen oder einzelnen Nanoteilchen zu erhalten. Es handelt sich bei dieser Anlage um die weltweit zweite Installation nach der TU Delft. Die Aufrüstung erfolgte mit Hilfe eines speziellen Kooperationsprojektes mit FEI (Eindhoven) und Gatan (USA), das vom Forschungsförderungsfonds der Gewerblichen Wirtschaft in Wien und von der Steiermärkischen Landesregierung in Graz gefördert wurde.

Die Gesamtanlage erforderte im Zeitraum 2000 bis 2003 Investitionen in der Höhe von etwa 1,75 Mio E, die zu 25 % von der TU Graz und zu 75 % vom Verein zur Förderung der Elektronenmikroskopie und Feinstrukturforschung über Projektförderungen aufgebracht wurden.

- **Niederdruck-Rasterelektronenmikroskop (Environmental SEM = ESEM)**

Das für unser Institut herausragende Ereignis des letzten Jahres war die Lieferung eines Niederdruck-Rasterelektronenmikroskops (Juni 2002), wodurch eine Reihe von neuen wichtigen Untersuchungsmethoden am Institut verfügbar werden. Dieses neue Instrument wird für die Charakterisierung von „feuchten“ Materialien bei hoher Auflösung eingesetzt und wird mit einer Kühl-, Heiz-, Zug- und Druckbühne ausgerüstet. Aus diesem Grund ist das Mikroskop sehr gut für in-situ Untersuchungen geeignet, wie zum Beispiel für das Studium von Phasenübergängen, Hochtemperaturverhalten,

Eintrocknungsvorgängen u.v.a. mehr. Einsatzbereiche werden vor allem in der Technischen Chemie, Biochemie und Biotechnologie liegen. Das Mikroskop wird von FEI Eindhoven geliefert und wird im April 2003 mit einer Feldemissionskathode aufgerüstet. Für die Realisierung mussten finanzielle Aufwendungen von über 0,7 Mio Euro erbracht werden: Zur Hälfte wurde das Projekt durch den Verein zur Förderung der Elektronenmikroskopie mit Unterstützung durch die Steirische Wirtschaftsförderung (SFG) und der Wachstumsförderung des Bundesministeriums für Wirtschaft und Arbeit (BMWA) finanziert. Die andere Hälfte konnte von der TU Graz im Rahmen eines speziellen vom Rat für Forschungs- und Technologieentwicklung (RFT) empfohlenen Projektes aufgebracht werden.

- **„Focussed Ion Beam“ Anlage (FIB)**

2002 stand im Zeichen der Anstrengungen die Finanzierung zum Kauf einer dringend benötigten FIB-Anlage zustande zu bringen. Dies gelang mit Hilfe des Rates für Forschungs- und Technologieentwicklung (RFT), der das eingereichte Projekt positiv beurteilte. Nach umfangreichen Vergleichsmessungen entschieden wir uns im Oktober 2002 für den Ankauf einer FIB-Anlage (DUALBEAM) von FEI Eindhoven, die auf das spezielle Anforderungsprofil des Institutes angepasst wird. Die Anlage wird im Juni 2003 am Institut installiert werden.

### **1.3. Die wichtigsten wissenschaftlichen Ergebnisse**

Im folgenden werden einige wichtige Forschungsergebnisse zusammengefasst, die während der Berichtsperiode erarbeitet worden sind. Die meisten von ihnen wurden bereits in namhaften internationalen wissenschaftlichen Zeitschriften publiziert.

- Grundlegende Arbeiten zur räumlichen Auflösung der Energiefilterungs-Transmissionselektronenmikroskopie (EFTEM) in Zusammenarbeit mit dem Nationalen Zentrum für Elektronenmikroskopie (NCEM am LBNL in Berkeley (USA).
- HREELS von Übergangsmetalloxiden (Kooperation mit Gatan Inc, USA; FEI, Eindhoven, Niederlande, dem Fritz-Haber-Institut in Berlin und der TU Delft, Niederlande).
- Entwicklung neuartiger Auswertetechniken für Spektrum-Imaging mit EELS wie z.B. „Elemental occurrence maps“.
- Entwicklung einer nasschemischen Methode für die Präparation von metallischen Nanoteilchen.
- Erfolgreiche Präparation von oxidischen Nanoteilchen, die aus zwei Komponenten bestehen, in Zusammenarbeit mit VTT, Espoo (Finnland).
- Entwicklung einer neuen EFTEM-Abbildungsmethode für die Detektion von Nanometer dünnen Oxidschichten in Halbleiterbauelementen.
- Einführung der Rückstreu-Elektronenbeugung (EBSP) im Rasterelektronenmikroskop am Institut und erste erfolgreiche Problemlösungen in Zusammenarbeit mit dem Institut für Werkstoffkunde und Schweißtechnik der TU Graz.
- Entwicklung einer neuen Methode für die Bestimmung der Orientierung und Kristallinität von Polypropylen mittels Mikro-Ramanspektrometrie.
- Erfolgreiche Charakterisierung von vielen in Entwicklung befindlichen Werkstoffen, z.B. von Stählen mit nanometergroßen Ausscheidungen, von nanostrukturierte Beschichtungen und Nanoteilchen, teilweise in Zusammenarbeit mit dem Instituto de the Instituto de Ciencia de Materiales in Sevilla, Spanien.

### **1.4. Ereignisse und Aktivitäten im Zeitraum 2001-2002**

Der Berichtszeitraum war geprägt von den enormen Anstrengungen, die Instrumentierung zu

verbessern und den Personalstand zu halten bzw. sogar zu erweitern. Aufgrund der speziellen Institutsstruktur ist es aber gelungen, viele Schwierigkeiten zu überwinden. Dank der breiten Streuung der Projekte und Partnerschaften konnten wir sogar die Zahl der Doktoranden und damit den Mitarbeiterstab insgesamt deutlich erhöhen.

#### Personal:

Wie in den beiden vorhergehenden Jahren war die Fluktuationsrate bei den Mitarbeitern hoch, und aufgrund aktueller Entwicklungen bei der Neuorganisation der österreichischen Universitäten ist zu erwarten, dass sich dies auch in Zukunft fortsetzen wird.

- Der stellvertretende Institutsvorstand, Ass.-Prof. Dipl.-Ing. Dr.techn. Peter GOLOB, trat am 28. Februar 2001 in den Ruhestand. Dr. Golob leitete die Arbeitsgruppe „Mikrobereichsanalytik und Rasterelektronenmikroskopie“, war seit 1968 Angehöriger des Institutes und seit 1. Jänner 1989 stellvertretender Institutsvorstand.
- Ing. Hans Waltinger trat am 1. Juni 2001 in den Ruhestand. Ing. Waltinger leitete die Arbeitsgruppe für „Rasterelektronenmikroskopie“; er war seit 1970 am Institut beschäftigt.
- Frau Daniela Rauchenwald schied mit 30. Jänner 2002 aus dem Dienstverhältnis mit dem ZFE Graz.
- Ing. Adolf Aldrian tritt am 31. Dezember 2002 in den Ruhestand. Ing. Aldrian leitete die Arbeitsgruppe „Geräteentwicklung“ und war seit 1960 am Institut angestellt.
- Dr. Werner Grogger kam am 1. März 2001 von einem 1 ½ jährigen Forschungsaufenthalt am National Center for Electron Microscopy am LBNL (Berkeley, USA) zurück (Max-Kade Stipendiat).
- Frau Sanja Simic ist seit 15. Mai 2001 beim ZFE Graz angestellt und arbeitet in der Gruppe von Dr. Pölt.
- Frau Margit Wallner ist seit 1. Jänner 2002 beim ZFE Graz angestellt und arbeitet im Fotolabor des Institutes (Gruppe DI Zedlacher).
- Herr Christian Brandl ist seit 1. April 2002 im Rahmen in der Teilrechtsfähigkeit des FELMI in der Arbeitsgruppe von Dr. Wilhelm angestellt.
- Herr Manuel Paller ist seit 1. Juli beim ZFE Graz in der Arbeitsgruppe von Dr. Warbichler angestellt.
- Herr MMag. Werner Rechberger ist seit 1. Juni 2002 im Rahmen der Teilrechtsfähigkeit des FELMI in der Arbeitsgruppe von Dr. Hofer angestellt und beschäftigt sich mit der Nanoanalytik von Stählen und Legierungen.
- Herr Dipl.-Ing. Bernhard Schaffer ist seit 1. September 2002 im Sonderforschungsbereich „Elektroaktive Stoffe“ angestellt und arbeitet am FELMI in der Arbeitsgruppe von Dr. Hofer an der Charakterisierung von elektroaktiven Materialien.
- Herr Dipl.-Ing. Michael Toth ist seit 1. Oktober 2002 im Rahmen der Teilrechtsfähigkeit des FELMI in der Arbeitsgruppe von Dr. Hofer angestellt und beschäftigt sich mit der Entwicklung von Nanostrukturen.
- Herr Dipl.-Ing. Armin Zankel ist seit 1. November 2002 im Rahmen der Teilrechtsfähigkeit des FELMI in der Arbeitsgruppe von Dr. Pölt angestellt und beschäftigt sich mit der Entwicklung von in-situ Untersuchungen im neuen ESEM.
- Dr. Mario Schmied wurde beim TÜV Österreich zum Qualitätsmanager ausgebildet.
- Dr. Ilse Papst absolvierte den Kurs an der Verwaltungsakademie des Bundes in Wien.
- „Outstanding Poster Award“ für Dipl.-Ing. Andreas Gupper auf der FACSS 2002 in Providence, USA.
- Dr. Mario Schmied erhielt für seine Dissertationsarbeit, die im Februar 2002 abgeschlossen wurde, einen Förderungspreis von der Fa. Anton Paar, Graz.

### Die wichtigsten im Zeitraum 2001-2002 erworbenen Geräte:

Im Rahmen der Kooperation zwischen FELMI und ZFE konnten wesentliche Investitionen gemeinsam durchgeführt werden, z.B.

- Analytisches Hochauflösungs-Transmissionselektronenmikroskop: TECNAI F20 von FEI (Eindhoven) mit FEG, HR-STEM mit HAADF-Detektor, Energiedispersivem Röntgenspektrometer (EDXS), einem Hochauflösungs-Energiefilter und einem Monochromator; Finanzierung durch TU Graz, Verein zur Förderung der Elektronenmikroskopie mit Unterstützung durch den Forschungsförderungsfonds der Gewerblichen Wirtschaft, Wien, Steiermärkische Landesregierung Graz und Wachstumsförderung des Bundesministeriums für Wirtschaft und Arbeit, Wien.
- Hochauflösungs-Rasterelektronenmikroskop (Nieder-Vakuum Gerät mit Feldemissions-Kathode), mit EDX-Spektrometer, Heizbühne und Zug- und Druckbühne; Finanzierung durch Verein zur Förderung der Elektronenmikroskopie mit Hilfe der Steirischen Wirtschaftsförderung (SFG), der Wachstumsförderung des Bundesministeriums für Wirtschaft und Arbeit, Wien und durch das Projekt, das vom Rat für Forschungs- und Technologieentwicklung, Wien genehmigt wurde.
- FT-Infrarot-Mikroskop der Fa. Bruker mit Spezialobjektiven (oberflächennahe Analyse mit ATR, dünne Schichten mit GIR), vorbereitet für den Ausbau zu einem bildgebenden System (FPA Imaging Detektor); Finanzierung durch TU Graz über das Projekt, das vom Rat für Forschungs- und Technologieentwicklung (RFT), Wien genehmigt wurde.
- CCD-Kamera von Gatan für das Transmissionselektronenmikroskop Philips TEM420 (unterstützt durch Wachstumsförderung des Bundesministeriums für Wirtschaft und Arbeit, Wien).
- Lichtmikroskop „Infinite Focus“ von Alicona (Grambach) für die automatische Bildanalyse von ausgedehnten Probenbereichen unter erweiterter Schärfentiefe.
- Aufbau einer Niederenergie-Ionendünnungs-Apparatur basierend auf einer Anlage des ZFE Graz mit neuen Ionenkanonen von Technoorg Linda (Budapest) für die TEM-Probenpräparation (ZFE Graz).
- Installation einer elektrolytischen Dünnungsanlage Struers für die TEM-Probenpräparation (Wachstumsförderung des Bundesministeriums für Wirtschaft und Arbeit, Wien).

### Einbindung in die wissenschaftliche Gemeinschaft:

- F. Hofer ist Mitglied des Herausgeberrates von MICRON (Internationale Mikroskopie-Zeitschrift), Vorstandsmitglied der Österreichischen Gesellschaft für Elektronenmikroskopie (ASEM) und stellvertretender Aufsichtsrats-Vorsitzender der Fa. Anton Paar in Graz.
- F. Hofer war Mitglied des wissenschaftlichen Beirates der Dreiländertagung für Elektronenmikroskopie in Innsbruck, Österreich (2001) und des internationalen Kongresses für Elektronenmikroskopie (ICEM) in Durban, Südafrika (2002).
- Mitarbeiter des Institutes waren als Gutachter für folgende Institutionen bzw. wissenschaftliche Zeitschriften tätig:  
VolkswagenStiftung Hannover, BRD; Netherlands Organization for Scientific Research (NOW); Institut für Festkörper- und Werkstoffforschung, Dresden, BRD; University of Cambridge, U.K., University of Antwerpen, Belgium.  
Ultramicroscopy, Microscopy & Microanalysis, Micron, J. Microscopy, J. Electron Microscopy, Mikrochimica Acta, Monatshefte f. Chemie, Chemistry of Materials, Spectrochimica Acta B, Philosophical Magazine A, Vacuum, Applied Physics Letters, Physical Review Letters, Macromolecular Symposia.

- G. Kothleitner ist seit 2002 Mitglied des Beirates der Arbeitsgruppe „EFTEM&EELS“ in der Deutschen Gesellschaft für Elektronenmikroskopie (DGE).
- Organisation eines international besetzten Symposium an der TU Graz am 12. Juni 2001 aus Anlass des 50-jährigen Bestehens des Institutes und der Übergabe des neuen Hochauflösungselektronenmikroskops.
- Intensive Zusammenarbeit mit Forschungsgruppen der Steirischen Universitäten im Spezial-Forschungsbereich „Elektroaktive Stoffe“ seit Mai 1999.
- Internationale EELS-EFTEM School im November 2002 mit Teilnehmern aus Großbritannien, Norwegen, Österreich und China.
- Das FELMI arbeitete an der Gestaltung des neuen Universitätslehrganges der TU Graz „Nanotechnologie und Nanoanalytik“ aktiv mit.
- Kooperation mit dem Material Center Leoben und dem im Aufbau befindlichen ABC-Kompetenzzentrum an der TU Graz.
- Kooperation mit mehreren Europäischen Instituten von Sevilla bis Helsinki im Rahmen des Programmes COST523 „Nanostructured materials“.
- Erfolgreiche Teilnahme des Institutes an der Präsentation der TU Graz an der Hannover Industriemesse im April 2001.
- Erfolgreiche Teilnahme des Institutes an der MATERIALICA in München im Oktober 2002 in Zusammenarbeit mit der Steirischen Wirtschaftsförderung (SFG).
- Weitere Zunahme der Zahl der eingeladenen Vorträge von Institutsmitgliedern im Ausland, wobei die Aktivitäten von Amerika über Europa bis Australien und China reichen.
- Das ZFE ist Mitglied der Austrian Cooperative Research (ACR) und betreibt wissenschaftliche Zusammenarbeit mit mehreren anderen ACR Instituten.

#### Das Institut in den Medien

- *Kleine Zeitung*, 10. Juni 2001.  
„Eine Superlupe für Steirer“
- *ORF-Bericht in „Steiermark Heute“*, 15. Juni 2001.
- *Jahresbericht 2000/01 TU Graz*  
„Seeing the Invisible: Mikroskopie mit atomarer Auflösung“
- *Kleine Zeitung*, 6. Jänner 2002  
„Bizarre Reise in die Tiefe“
- *Forschungsjournal der TU Graz WS 2001/02*  
„Seeing the Invisible“
- *VIA Airportjournal Graz 5/2002*  
„Graz sieht mehr: Mit dem ersten Hochauflösungselektronenmikroskop Österreichs“

#### **1.5. Pläne für die Zukunft**

Die Verwertung und Ausdehnung der Potentiale der nunmehr bestehenden Instrumentierung sowie neue zukunftsweisende Verfahren aufzubauen ist für das Institut von größter Bedeutung. Erweiterungsinvestitionen sollten sich vor allem auf folgende Entwicklungen fokussieren:

- FPA-Detektor für das neue FT-Infrarot-Mikroskop von Bruker
- Focussed Ion Beam System für die elektronenmikroskopische Probenpräparation vorwiegend für Halbleiterbauelemente und Beschichtungen von Werkstücken (Lieferung im Juni 2003).
- Hochauflösungs-Rasterelektronenmikroskop (geplant für 2005).
- Rasterkraftmikroskopie in Verbindung mit der Rasterelektronenmikroskopie (geplant für 2004).

- Laufender Ersatz von veralteten Geräten, die noch für Routinearbeiten im Einsatz stehen, wie z.B. alte EDX-Spektrometer oder spezielle Computerkomponenten.

Neben einer verstärkten Kooperation mit anderen Instituten der Steirischen Hochschulen, so z.B. im Rahmen eines geplanten Sonderforschungsbereiches „Nanokomposites“, bemühen wir uns über Kooperationen mit namhaften Forschungsinstituten aus aller Welt den Austausch von Wissenschaftlern zu verstärken.

Gegenwärtig wird ein von Prof. Dr. Christian Colliex (Univ. Paris-Sud, Frankreich) koordiniertes „Network of Excellence“ im Bereich Transmissionselektronenmikroskopie (TEMNET) für die Eingabe im 6. Rahmenprogramm der EU vorbereitet. Das FELMI koordiniert den Mitteleuropa-Knoten des geplanten Netzwerkes, der die Länder Österreich, Ungarn und Slowenien umfassen wird.

In den nächsten Jahren werden wir auch versuchen verstärkt Kongresse und Tagungen in die Steiermark zu bringen: Für 2003 planen wir die Durchführung eines Workshops mit dem Thema „EELS of STEELS“ und 2005 wird das Institut den internationalen EELS-EFTEM Workshop organisieren.

## 2.6. Dank

Das experimentelle Arbeiten auf dem Gebiet der Hochauflösungselektronenmikroskopie in einem Forschungsinstitut wie dem unseren setzt über die volle Motivation aller Mitarbeiter auch beträchtliche finanzielle Unterstützung voraus. Ohne die Hilfe vieler Institutionen wäre es nicht möglich gewesen, die Instrumentierung, die Kooperationen und die Resultate, wie sie in diesem Leistungsbericht geschildert werden, zu erreichen. Im Berichtszeitraum schulden wir daher besonderen Dank den Repräsentanten unserer Universität, Rektor O.Univ.-Prof. Dr. Erich Hödl, den Vizerektoren Hofrat Dr. Johann Theurl und O.Univ.-Prof. Dr. Hans Sünkel sowie der zentralen Universitätsverwaltung.

Finanzielle Unterstützung unserer Arbeit wurde in der Hauptsache durch fördernde Organisationen gewährt, vor allem durch den Forschungsförderungsfonds der gewerblichen Wirtschaft (FFF), den Forschungsförderungsfonds der wissenschaftlichen Forschung (FWF), über die Austrian Cooperative Research (ACR) das Bundesministerium für Wirtschaft und Arbeit in Wien, der Steirischen Wirtschaftsförderung (SFG), die Steiermärkische Landesregierung (Landesrat Dipl.-Ing. Leopold Schögg) und durch unsere Kooperationspartner aus der Industrie sowie aus dem Universitätsbereich hierzulande und im Ausland.

Ausdrücklich danken wir auch Prof. Dipl.-Ing. Helmut List, Komm.Rat. Dipl.-Ing. Ulrich Santner und Komm.Rat Dr. DDipl.-Ing. Helmut Katzenberger, die zur Unterstützung unserer Arbeit viel von ihrer wertvollen Zeit für ihre Tätigkeit im Verein zur Förderung der Elektronenmikroskopie aufgewendet haben.



Participants of the EELS-EFTEM School at the Institute, November 2002.

From the first “Institutstag” of the FELMI-ZFE in the Brauhaus Puntigam, November 6, 2001



Dr. Grasenick,  
DI Zedlacher,  
Dr. Warbichler  
(from right)

## 2. Verein zur Förderung der Elektronenmikroskopie und Feinstrukturforschung

The industrial associates organisation was established in 1959 to support the institute and to facilitate greater interaction between industrial and academic scientists. On the one hand the "Verein" supported the institute in terms of improvement of instrumentation thus enabling state-of-the-art instrumentation (at least partly) which was always very important because of the limited resources of the university. On the other hand it allowed to maintain a high skilled and well trained permanent staff in the Center for Electron Microscopy Graz (ZFE Graz). The ZFE Graz is member of the "Austrian Cooperative Research" (ACR) organisation. The program of the ZFE Graz is designed to provide industry with useful results from established and emerging new microscopy techniques and to keep the in-house specialists in industry in touch with the latest developments in the field.

Policies and procedures of the "Verein" and the ZFE Graz are established by a steering committee consisting of academic and industrial scientists. Since 1995 the "Verein" is headed by Professor Dipl.-Ing. Helmut LIST (AVL Graz) and presently the "Verein" has 28 members mainly from Austria. Since the last general business meeting on February 28, 2002 the administrative body for the next six years is given as follows:

### **Präsidium / Presidential Committee:**

Präsident / President:	Prof. Dipl.-Ing. Dr-Ing.h.c. Helmut LIST
1. Stellvertreter des Präsidenten /	
1. Vice president:	Komm. Rat Dipl.-Ing. Ulrich SANTNER
2. Stellvertreter des Präsidenten /	
2. Vice president:	Komm. Rat DDipl.-Ing. Dr. Helmut KATZENBERGER

### **Vorstand / Managing Committee:**

Vorsitzender / Head:	Komm. Rat Dipl.-Ing. Ulrich SANTNER
Finanzreferent / Financial referee:	DDr. Wilfried SCHÖNAUER
Vertreter der TU Graz /	
Representative of TU Graz:	O. Univ.-Prof. Dr. Hartmut KAHLERT
Leiter des / Head of ZFE Graz:	Ao. Univ.-Prof. Dipl.-Ing. Dr. Ferdinand HOFER

### **Rechnungsprüfer / Controller:**

1. Rechnungsprüfer:	Dr. Hermann PUCHER
2. Rechnungsprüfer:	Mag. Andrea DOLLESCHAL

### **Wissenschaftlicher Beirat / Scientific Board:**

- Univ.-Prof. Dipl.-Chem. Dr. Jürgen BESENHARD, TU Graz
- Univ.-Prof. Dipl.-Ing. Dr. Horst CERJAK, TU Graz
- Univ.-Prof. Dipl.-Ing. Dr. Harald P. FRITZER, TU Graz
- Univ.-Prof. Dr. Georg HOINKES, Universität Graz
- Univ.-Prof. Dipl.-Ing. Dr. Franz JEGLITSCH, Montanuniversität Leoben
- Univ.-Prof. Dr. Hartmuth KAHLERT, TU Graz
- Univ.-Prof. Dr. Klaus LEDERER, Montanuniversität Leoben
- Univ.-Prof. Dr. Maria-Anna PABST, Universität Graz
- Univ.-Prof. Dipl.-Ing. Dr. Franz STELZER, TU Graz

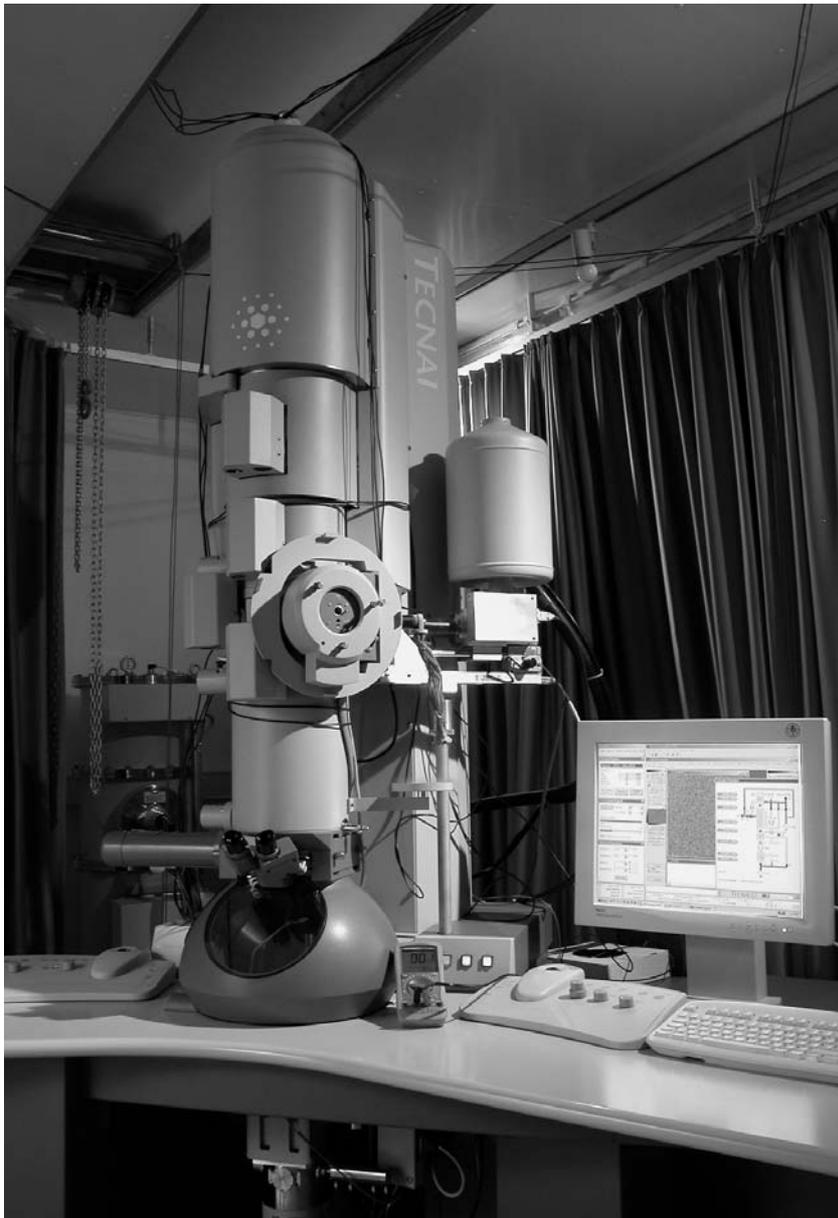
### Wirtschaftlicher Beirat / Economic advisory Board

Komm. Rat Dr. Theo GUMPELMAYER, ACR Wien  
 Dipl.-Ing. Dr. Armin HOLZNER, Semperit Techn. Produkte, Wimpassing  
 Dkfm. R. KOLITSCH, Graz  
 Dipl.-Ing. Dr. Wolfgang NEISSL, Borealis AG, Linz  
 Prof. Dr. Bernhard PELZL, Joanneum Research, Graz  
 Min. Rat Dr. K. PERSY, Bundesministerium für Bildung, Wissenschaft u. Kultur, Wien  
 Dipl.-Ing. Christian RAINER, Omya, Gummern  
 Vizerektor Dipl.-Ing. Dr. Johann THEURL, TU Graz

### Members of the “Verein zur Förderung der Elektronenmikroskopie”

 Austria Micro Systems AG Unterpremstätten	 OMYA AG Oftringen, Schweiz
 Austria Technologie & Systemtechnik Leoben	 OMYA GmbH Gummern
 AVL List GmbH Graz	 Plansee AG Reutte
 BC Components Austria GmbH Klagenfurt	 Porzellanfabrik Frauental GmbH Frauental
 Böhler Edelstahl GmbH & Co KG Kapfenberg	 Semperit AG Holding Wimpassing
 Borealis GmbH Linz	 Solutia Austria GmbH Graz
 Birgl & Bergmeister Papierfabrik GmbH Niklasdorf	 Solvay Österreich GmbH Ebensee
 EPCOS OHG Deutschlandsberg	 Tann Papier GmbH Traun
 Forschungsinstitut f. Elektronenmikroskopie Graz	 Technische Universität Graz
 Ingenieurbüro Steiner Leoben	 Teich AG Weinburg

 Industriellenvereinigung Graz	 Treibacher Auernet GmbH Treibach-Althofen
 Infineon Technologies Austria AG Villach	 TÜV Österreich Wien
 Joanneum Research Graz	 Veitsch Radex GmbH-RHI Breitenau
 MAG Maschinen- und Apparatebau AG Graz	 Voith Paper Service GmbH Wimpassing
 www.UNILEOBEN.AC.AT Montanuniversität Leoben	 Wirtschaftskammer Steiermark, Graz



The analytical high resolution electron microscope TECNAI F20; already equipped with the monochromator, the HR-energy-filter and the EDX-spectrometer.

### 3. Institute Representatives and Staff / Personalstand

**Head of Department** HOFER Ferdinand, Dipl.-Ing. Dr.techn., ao.Univ.-Prof.  
KOTHLEITNER Gerald, Dipl. Ing. Dr.techn. (since March 2001)

**Scientific Staff** Aldrian Adolf, Ing.  
Brunegger Albert, Ing.  
Grogger Werner, Dipl. Ing. Dr.techn.  
Ingolic Elisabeth, Dr.phil.  
Letofsky-Papst Ilse, Dipl. Ing. Dr. mont.  
Pölt Peter, Dipl. Ing. Dr.techn.  
Rom Irmgard, Dipl. Ing. Dr.techn.\*\* (until April 2001)  
Schmied Mario, Dipl. Ing. Dr.techn.  
Schröttner Hartmuth Ing.  
Wagner Julian, Dipl. Ing. (since August 2001)  
Waltinger Hanns (retired July 2001)  
Warbichler Peter, Dipl. Ing. Dr.techn.  
Wilhelm Peter, Dr.phil.  
Zedlacher Harald, Dipl. Ing.

**PhD students** Schaffer Bernhard, Dipl. Ing. \*\* (since Oct. 2001)  
Gupper Andreas, Dipl. Ing. \*  
Mitsche Stefan, Dipl. Ing.\*  
Mitterbauer Christoph, Dipl. Ing.\*\*  
Rechberger Werner, Mag. Mag. \*\* (since June 2002)  
Toth Michael, Dipl. Ing. \*\* (since October 2002)  
Zankel Armin, Dipl. Ing. \*\* (since November 2002)

**General Staff** Arnusch Denise, Image lab-apprentice (since Sept. 2002)  
Bahr Peter, EM-Operator  
Birstingl Gerhard, Mechanic  
Brandl Christian, EM-Operator \*\* (since March 2002)  
Brunegger Margit, Chem.lab-assistant \*  
Czapek Wolfgang, Mechanic \*  
Dienstleder Martina, Chem.lab-assistant \*  
Elis Christof, EM-Operator  
Fauland Evelyn, Mech.-apprentice (finished April 2001)  
Fleischhacker Caroline, Chem.tech.-assistant \*\* (maternity leave since December 2001)  
Freund Angela, Cleaner  
Goger Sabine, Secretariat \*  
Gusmagg Anneliese, Secretariat \*  
Kortschak Elisabeth, Chem.tech.-assistant \* (since Dec. 2001)  
Kranzbinder Elke, Cleaner  
Markovic Helmut, Image Processing  
Oberbichler Martin, Mech.-apprentice (finished April 2001)  
Paller Manuel, Chem.lab-assistant \* (since June 2002)  
Rauchenwald Daniela, Image processing \* (until Febr. 2002)  
Roßmann Anita, Chem.lab-apprentice (since Sept. 2001)  
Seidl Emanuel, Mech.-apprentice (since Sept. 2001)  
Simic Sanja, EM-Operator \* (since May 2002)  
Streussnig Fatima, Secretariat \*  
Wallner Margit, Image lab \* (since January 2002)  
Windisch Gerhard, Design, PC- & LAN-Admin.

\* ZFE staff, \*\* supported by projects and „Teilrechtsfähigkeit“ of the FELMI

**Guests**

EGERTON Ray, Prof., Dr. University of Edmonton, Alberta, Canada.  
POPA Marius, Dr., Mineralogy Department, Univ. Bukarest, Rumania.  
PARAMESWARAN Padmanabhan, Materials Characterisation Group,  
Indira Gandhi Centre for Atomic research, Kalpakkam, India.



## 4. Laboratory Facilities and Highlights of Equipment / Laboreinrichtungen und wichtigste Instrumente

### Scanning Electron Microscopes

- Analytical high resolution SEM: LEO Gemini DSM986  
0.1-30 kV, field emission gun, with EDX detector Noran Voyager 3105A, with TSL EBSD detector, micro hardness tester (Anton Paar) and cryogenic specimen transfer system (developed at FELMI-ZFE)
- Environmental Scanning Electron Microscope (ESEM): FEI Quanta 200 equipped with Noran Vantage EDX system, heating stage (up to 1500°C), Peltier cooling-stage
- Analytical SEM: Philips SEM505  
1-30kV, LaB<sub>6</sub> cathode, EDX detector DX4 (EDAX) with ultrathin window and Micro-spec WDX system 2A with multilayer crystals
- Scanning electron microscope: Leitz AMR 1600, 1-30kV, W-cathode
- Specimen stages for cryo-investigations, micro x-ray fluorescence and x-ray microscopy (developed at FELMI-ZFE)

### Transmission Electron Microscopes (TEM)

- Analytical high resolution TEM: FEI TECNAI F20  
200kV, field emission gun, supertwin objective lens, STEM (0.2 nm probe) with HAADF detector, with EDX Si(Li) light element detector (EDAX) and High Resolution Gatan Imaging Filter (HRGIF) with 1kx1k CCD camera
- Analytical TEM: Philips CM20  
200kV, LaB<sub>6</sub> cathode, twin lens, STEM with SE detector and Gatan BF/DF detector, EDX detector (HPGe, Noran) and Gatan Imaging Filter (including a 1kx1k CCD camera)
- Analytical TEM: Philips EM420  
120 kV, LaB<sub>6</sub> cathode, twin lens, STEM with BF/DF, SE and BSE detectors and EDX Si(Li) detector with Be window (EDAX), low dose unit, CCD-camera
- Specimen holders: Philips double tilt holder, Philips cryo-transfer and cooling holder Gatan double tilt cooling holder for analytical work, low background holders, rotation and heating holders

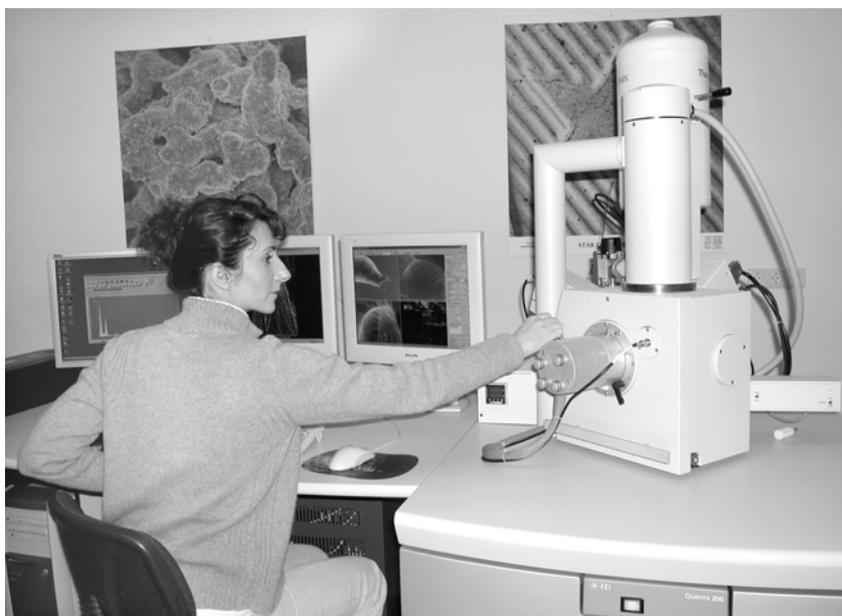
### Further Instrumentation

- FT-IR microscopes: Bruker Equinox 55 spectrometer with Hyperion 3000 microscope, ATR objective (Ge crystal), Grazing Angle Objective, Miracle single reflection horizontal ATR unit (diamond and Ge crystal), Sadtler KnowItAll spectral libraries and search software. Spectra-Tech Advanced Analytical Microscope with ATR objective (ZnSe and Ge crystals), attached to a Bomem MB series spectrometer.
- Raman microscope: Renishaw system 2000, including Leica DMLM research microscope, with dual laser system: diode laser (782 nm, 25 mW) and HeNe laser (633 nm, 17 mW), holographic notch filters, CCD detector, motorized xyz stage for mapping and confocal experiments, Raman imaging, electrochemical cell, hot-cold stage.
- Light microscope: Zeiss Axioplan for observation with transmitted and reflected light with brightfield, darkfield, polarization, interference contrast (DIC), phase contrast and a Polaroid DMC Digital Microscope Camera.
- Stereo light microscope Leica M Z 6 for sample-preparation
- Light microscope METAVAR (Reichert)

- Light microscope: 3D Infinite Focus (ALICONA)

### Electron microscopical preparation equipment

- Diamond Saw (Well)
  - Diamond Saw ISOMET 1000 (Buehler)
  - Minimet Polisher (Buehler)
  - Ultrasonic disc cutter (Gatan)
  - Dimple Grinder (Gatan)
  - Tripod Polisher (Southbay Technology)
  - Electrolytic thinning device (Struers TenuPol 5)
  - Low angle ion milling apparatus (developed at FELMI-ZFE), equipped with low energy ion guns (Technoorg.-Linda)
  - Ion milling and polishing system PIPS with digital zoom camera (Gatan)
  - Sawing microtome (Leitz)
  - Milling cutter (Reichert-Jung)
  - Ultramicrotome: OmU3 (Reichert-Leica)
  - Ultramicrotome: Ultracut UCT with EM FCS for low-temperature sectioning (Leica)
  - Microtome Supercut 2050 for light microscopy thin sections
  - Ultramicrotome Ultracut E (Reichert-Leica)
  - Clean air facility DLF (Wörden)
  - Plasma Cleaner (ZFE development)
  - Etching and Sputtering Coater GEA005 (ZFE development)
  - Cryo-preparation system EPA 101 with quadrupol mass spectrometer QMG311 (ZFE development)
  - Evaporation and sputtering apparatus (ZFE development)
  - Preparation system EPA101 (ZFE development)
  - Electron beam evaporators (Leybold, Balzers)
  - Experimental electron microscopical preparation system based on EPA101 (ZFE development)
- Computer network with 55 computers (PC, Mac, Unix)
  - High quality printers for photographs



Sanja Simic uses the new  
“Environmental Scanning  
Electron Microscope”  
(ESEM)  
FEI Quanta 200

## 5. Academic Education / Lehrveranstaltungen

provided by the FELMI staff at the TU Graz

No.	Sem.	Title	Type	Lecturer
303.018	WS	Electron Microscopy in Materials Science	2 V	G. Kothleitner
46 03 60*	WS	Physics Laboratory Course	6 P	I. Letofsky-Papst
513.010/11/12	WS/SS	Applied Physics Laboratory Course	5 P	J. Wagner
513.038	WS	Electron Microscopy in Solid State Physics I	2 V	W. Grogger
513.039	SS	Electron Microscopy in Solid State Physics II	2 V	W. Grogger
535.065	WS	Analytical Electron Microscopy	2 V	F. Hofer
535.066	SS	Materials Characterization using Electron Microscopy	2 P	G. Kothleitner
535.067	WS	Special Aspects of Analytical Electron Microscopy	3 Se	F. Hofer
535.068	SS	Special Aspects of Analytical Electron Microscopy	3 Se	F. Hofer
535.069	SS	Structure Analysis by High Resolution Electron Microscopy	2 V	F. Hofer

\* in cooperation with the Institute of Physics, Montanuniversität Leoben, Austria

The first "EELS-EFTEM School" of the FELMI was launched in November 2002 with participants from Norway, Denmark, Great Britain, China and Austria. Tours of the institute including lectures and demonstrations have additionally been offered for excursions of physics and chemistry teachers and for students from the TUG, schools and local universities.

Additionally, we have organised URANIA-lectures in November 2001 and 2002 presenting the achievements of "Electron Microscopy" to interested people from outside of the universities.

## 6. Diploma Theses and Doctoral Theses / Diplomarbeiten und Dissertationen

were performed in cooperation with other institutes of the TU Graz.

### Finished diploma thesis:

SCHAFFER Bernhard (July 2002): "Imaging of Ultrathin Silicon Dioxide Layers on Silicon with Energy Filtering Transmission Electron Microscopy" in cooperation with the "Institute of Solid State Physics".

### Finished doctoral thesis:

SCHMIED Mario, Dipl.-Ing. (March 2002): "Characterisation of Submicron Particles by Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry" in cooperation with the "Institute of Physical and Theoretical Chemistry".

**Doctoral theses in progress:**

GUPPER Andreas, Dipl.-Ing.: „Enhanced applications of microscopic characterisation techniques in materials science“

MITSCHE Stefan, Dipl.-Ing.: „Chemical and crystallographical characterization of submicron particles and thin layers in the scanning electron microscope “

MITTERBAUER Christoph, Dipl.-Ing.: „Investigations of nanostructured materials by using electron energy loss spectroscopy in the transmission electron microscope“

SCHAFFER Bernhard, Dipl.Ing.: „Characterisation of nanocrystalline, electro active materials by means of high resolution electron microscopy and energy filtering microscopy“

ZANKEL Armin, Dipl.Ing.: „In-situ experiments in the environmental scanning electron microscope“

TOTH Michael, Dipl.Ing.: „Electron microscopical investigation of nanoparticles and functional nanostructures“

RECHBERGER Werner, MMag.: „Characterising crystalline materials with high resolution scanning transmission electron microscopy and electron energy loss spectroscopy“



Dr. Peter Pölt presents a paper at the first “Institutstag” of the FELMI-ZFE in the Brauhaus Puntigam, 6. November 2001.

## **7. Main Research Areas of the Workgroups / Forschungsaktivitäten der Arbeitsgruppen**

The institute's main research activities are devoted to the study of the microstructure of all kinds of solids, materials and biological samples; e.g. alloys, steels, metals, ceramics, composites, minerals, polymers, nanoparticles, clusters, biological tissue. Additionally, members of the institute are actively involved in furthering the development of the methods serving these research areas. In 2001 and 2002 research funds were allocated by the FFF, ACR, the FWF within the Special Research program "Electroactive materials" and COST 523.

### **7.1. Microanalysis using scanning electron microscopy**

Scanning electron microscopy enables a nearly complete characterisation of a bulk specimen towards surface topography (also quantitative, including surface roughness by use of stereo images), chemical composition (EDXS, WDXS) and the crystallographic microstructure (EBSD).

In particular computer controlled SEM in combination with image processing enables the unattended analysis of both the geometrical and chemical parameters of thousands of individual particles down to a size of around 100 nm. This is used for the analysis of aerosols and fly ash particles e.g. in biomass heating plants. Another application is the determination of the size distribution of the modifier particles in modified polymers.

Many specimens, especially small environmental particles, experience strong specimen damage by electron irradiation. They change both their topography and their chemical composition. The basic mechanisms are not completely revealed now. Work is in progress to elucidate the fundamental reactions causing the damage.

Recently, the introduction of EBSD (electron backscatter diffraction) in the scanning electron microscope allows the identification of the crystal phase of microstructures and the determination of the orientation of individual crystallites. By scanning the specimen across selected areas of the specimen one obtains a full record of the microstructure of these areas. Subsequently grain size distributions can be calculated, texture analysis and quantification of partially re-crystallised polycrystals performed.

The conventional SEM operates in the high vacuum range. On the other hand the Environmental SEM (ESEM) permits pressures to around 10 Torr, and the use of different chamber gases. This makes the investigation of wet specimens possible. Additionally, by use of a heating stage (up to 1500°C), the specimen temperature can be varied. Thereby chemical reactions like corrosion of metals, electrolyte – solid interactions, but also the formation of alloys can be studied on a micrometer scale. Thus in the near future in-situ experiments in the ESEM will form an essential part of the research activities.

### **7.2. Nanoanalysis using analytical transmission electron microscopy**

The mechanical, chemical or electrical properties of different materials are not only determined by the crystal structure of the perfect material, but also by their defect structure. For example, the mechanical properties of steels depend on the type, size and distribution of precipitates, the strength of ceramics is monitored by the presence of impurity phases and the quality of semiconductor devices depends on the control of chemical and structural defects. A major research objective of the group is to correlate these physical properties to the microstructure of materials.

Transmission electron microscopy (TEM) allows to obtain structural information of most solid state materials (including polymers and biological tissue) down to an atomic scale. Due to its

almost continuous magnification range between 20x and 1.000.000x defects can be easily identified and studied. These investigations are supported or supplemented by analytical techniques such as electron energy-loss spectrometry (EELS), energy-filtering TEM (EFTEM) and energy-dispersive x-ray spectrometry (EDXS) which allow to analyse the elemental and chemical composition of thin samples down to a nanometer scale.

Research within the group is concentrated on improving techniques for recording EELS- or EFTEM data at high spatial resolution such as elemental mapping with EFTEM, EFTEM spectrum imaging. In a second step we focus on the development or improvement of new or existing data reduction methods, e.g. quantitative analysis of EELS spectra and/or EFTEM elemental maps, interpretation and simulation of near edge fine structures (ELNES) and extended energy-loss fine structures (EXELFS) for revealing chemical bonding information from nanometer sized specimen regions. In collaboration with groups from the University of Leeds (Rik Brydson) and the Vienna University of Technology (Peter Schattschneider) we have successfully started to simulate the ELNES structures.

The introduction of the second monochromated TEM system in the world which is able to record EELS spectra with high energy resolution thus offering chemical bonding information from nanometer sized specimen regions, will help to boost our research efforts in the field of nanoanalysis.

Furthermore, we try to increase the understanding of the interaction of high energy electrons with matter which is prerequisite for quantitative analysis using EELS and EFTEM or for understanding the ultimate limits for the characterization of chemistry at near atomic scale.

### **7.3. Raman- and FTIR microspectroscopy**

Infrared and Raman spectroscopy are powerful analytical techniques for the identification of organic and inorganic substances, based on the excitation of vibrations within the molecule. Coupled to a light microscope, small and complex samples can be analysed with high lateral resolution (IR: ca. 10  $\mu\text{m}$ , Raman: ca. 1-2  $\mu\text{m}$ ), whereby sample preparation – though not to be underestimated - in most cases can be kept to a minimum. Comprehensive spectral libraries enable the characterisation of polymers, fillers, gels, contaminations etc., thus complementing the results of X-ray spectroscopy (elemental composition) obtained in the electron microscope.

Independent scientific research within in the group is concentrated on the studies of polymers using micro Raman and infrared spectroscopy and imaging techniques. Control of polymer orientation and crystallinity is of high industrial interest in order to understand and improve the properties of plastic materials. Further studies are done on the morphology of polymer blends, and the thermal degradation of polyvinyl chloride.

### **7.4. Specimen preparation and apparatus development**

The institute has a long and well known tradition in the development of electron microscopical preparation equipment. Due to these efforts we have a high standard for the preparation of which is prerequisite for the successful application of electron microscopy in materials science. The efforts devoted in the sample preparation field are clear benefits for electron microscopy work!

During the last years we concentrated on the construction of auxiliary tools, such as developing a plasma cleaner for TEM-specimens. In projects underway we try to improve the preparation of TEM specimens by adapting the home built low angle ion milling device of the institute with low energy ion guns from Technoorg Linda (Budapest).



Dr. Peter Wilhelm working with the new FT-IR microscope Bruker Equinox 55 spectrometer with Hyperion 3000 microscope



Dr. Elisabeth Ingolic working with the new 3D Infinite Focus light microscope developed by ALICONA, Grambach, Austria

## 8. Projects at the FELMI-ZFE / FELMI-ZFE Projekte

- "Electron microscopical characterization of electroactive, nanostructured materials" Project F00923 within the Special Research Program "Electroactive Materials" and COST523 "Nanostructured materials" supported by FWF, Vienna, May 1, 1999 – April 30, 2005.
- "Improvement of nanoanalytical characterization techniques for the study of inner boundaries in materials" supported by FFF, Vienna, January 1, 2000 – June 30, 2003.
- „Study of polymer orientation with Raman microscopy“ supported by FFF, Vienna, September 1, 2000 – Mai 30, 2003.
- „Aerosols in biomass firing - characteristics, development and influence“ supported by „Bund-Bundesländer Kooperation“ (in cooperation with Univ.-Doz. Dr. J. Obernberger, Institut für Verfahrenstechnik, TU Graz) June 30, 1999 – July 1, 2001.
- "Orientation imaging microscopy and phase analysis of materials" supported by FFF, Vienna, November 1, 2000 – October 31, 2003.
- „Surface treatment of inorganic fillers for the modification of polymers“ supported by Federal Ministry for Education, Science and Culture (BMBWK), Vienna in cooperation with Univ.-Prof. Dr. Klaus Lederer, MU Leoben, January 1, 2000 – December 31, 2001.
- Project: „Wachstumsförderung“, arranged by ACR and supported by Federal Ministry for Economics and Labour (BMWA), Vienna, January 1, 1999 – December 31, 2003.
- „Multimethodenanalytik von Nanoteilchen“ supported by Steirischer Zukunftsfonds, in cooperation with MU-Leoben and KFU Graz, (start during 2003)
- „Neue Untersuchungsmethoden für Mikrosystemtechnik und Nanotechnologie“ supported by Federal Ministry for Education, Science and Culture (BMBWK), Vienna, recommended by the Rat für Forschung und Technologieentwicklung (RFT), June 1, 2002 – June 30, 2003.
- "Installation eines Hochauflösungs-Energiefilters und eines Monochromators am neuen analytischen Hochauflösungs-Elektronenmikroskop " supported by Steiermärkische Landesregierung, Fachabteilung 6A, November 1, 2001 – December 31, 2002.

## 9. Presentations at the Institute / Vorträge am Institut

29.3.2001: Prof. Dr. Klaus **WETZIG** (Institut f. Festkörper- und Werkstoffforschung, Dresden, Germany): „In situ-Untersuchungen der Elektromigration an Metallisierungsschichten mikroelektronischer Bauelemente im REM“

3.5.2001: Dr. Markus **GAHLEITNER** (Borealis, Linz, Austria): „Polypropylene – Material Development along the Chain of Knowledge“

28.5.2001: Prof. Dr. Robert **SCHLÖGL** (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abt. Anorgan.Chemie, Berlin, Germany): „In-situ Charakterisierung von polykristallinen Oxidkatalysatoren“

13.6.2001: Symposium „50 Years Electron Microscopy“ and “Introduction of the Analytical High Resolution TEM” at TU Graz:

Rik **BRYDSON** (Univ. of Leeds, UK): “Chemical information at high spatial resolution - Electron energy-loss spectrometry in the TEM”;

Phillipe-André **BUFFAT** (EPFL Lausanne, Switzerland): “Phase and structure determination in nanocrystals by electron diffraction contrast”;

Christian **COLLIEUX** (Univ. Paris Sud, France): “STEM investigation of nanotubes“;

Joachim **MAYER** (TU Aachen, Germany): “Energy-filtering TEM in physical sciences”;

Manfred **RÜHLE** (MPI Stuttgart, Germany): “High resolution electron microscopy of interfaces”;

Gustaaf van **TENDELOO** (RUCA Antwerpen, Netherlands): “TEM: How low can you go?”;

15.11.2001: DI. Gerhard **SCHINDELBACHER** (ÖGI, Leoben, Austria): „Gießen – ein flexibles Verfahren zur Herstellung hochkomplexer Bauteile“

6.12.2001: Dr. Ernst **LETOFSKY** (Inst. f. Werkstoffkunde, TU-Graz, Austria): „Elektronenmikroskopie zur Quantifizierung der Mikrostruktur am Beispiel hochwarmfester Kraftwerkstoffe“

10.1.2002: Prof. Miran **CEH** (Jozef Stefan Institute, Ceramics Department, Ljubljana, Slovenia): „High-resolution HAADF STEM Imaging of (Ca,Sr,Ba)TiO<sub>3</sub> Perovskites“

17.1.2002: Dr. Cecile **HEBERT** (Inst. f. Festkörperphysik, TU Wien, Austria): „ELNES Interpretation: Beispiele, Möglichkeiten und Grenzen“

14.2.2002: Dr. Dangsheng **SU** (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abt. Anorganische Chemie, Berlin, Germany): „ELNES and NEXAFS of Vanadium Oxides and Vanadium Phosphorus Oxides“

12.3.2002: Dr. Markus **LEICHT** (Infineon Technologies Villach, Austria): „Kristallstruktur- und Dotierstoff-Analytik von Halbleiter-Bauelementen; Infineon-Kooperationen mit Auftragglabors“

8.4.2002: Dr. Janos **OSAN** (Department of Health and Environmental Physics, KFKI Atomic Energy Research Institute, Budapest, Hungary): “Quantitative electron probe microanalysis of individual environmental particles using a reverse Monte Carlo Method”

15.5.2002: Prof. Ray **EGERTON** (University of Alberta, Edmonton, Canada): “The Future on Electron Energy Loss Spectrometry”

21.5.2002: Dr. Christelle **GREIN** (Borealis GmbH Research Area PP, Linz, Austria): „Impact modified isotactic polypropylene with controlled rubber intrinsic viscosities: some new aspects about morphology and fracture“

5.7.2002: Dr. Wilfried **SIGLE** (Max-Planck-Institut für Metallforschung, Stuttgart, Germany): “Neue Möglichkeiten und Anwendungen der analytischen Transmissions-Elektronenmikroskopie”

13.9.2002: Dr. Sergei **KAZARIAN** (Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London, UK): “Integrating Materials Process Engineering and Molecular Spectroscopy ”

17.10.2002: Dr. Stefan **SCHERER** (Alicona Imaging GmbH, Graz/Grambach, Austria): “3D Rekonstruktion und Analyse in der Mikroskopie”

16.12.2002: Prof. Dr. Peter **SCHATTSCHEIDER** (Institut für Angewandte und Technische Physik der TU Wien): "Inelastische Interferenzen im TEM: Plasmonen und Ionisationskanten"



Ing. A. Brunegger working with the ion milling apparatus developed at the FELMI-ZFE.

## 10. Publications of Members of the Institute Publikationen von Institutsmitarbeitern

### 2001

- R. Resel, N. Koch, F. Meghdadi, G. Leising, L. Athouel, G. Froyer, F. Hofer**  
 "A Polymorph Crystal Structure of Hexaphenylene Observed in Thin Films", Cryst. Res. Technol. 36 (2001) 47-54.
- F. Hofer, G. Kothleitner, P. Warbichler**  
 "Compositional mapping with energy filtering TEM: The present status", Microsc. Microanal. 7, Suppl. 2: Proceedings (2001) pp. 1136-1137.
- G. Kothleitner, F. Hofer, C. Trevor**  
 "Difference spectrum images: Numerical filters applied to EELS 3D data sets", Microsc. Microanal. 7, Suppl. 2: Proceedings (2001) pp. 1160-1161.
- A. Kulmburg, G. Kvas, G. Wiedner, P. Golob, P. Warbichler, M. Schmied, R.O. Bratschko**  
 "The microstructure of Co-Cr-Mo-(Nb) dental alloys", Prakt. Metallogr. 38 (2001) 514-531.
- M. Wachtler, M. R. Wagner, M. Schmied, M. Winter, J. O. Besenhard**  
 "The effect of the binder morphology on the cycling stability of Li-alloy composite electrodes", J. Electroanal. Chem. 510 (2001) 12-19.
- E. Bucher, W. Jantscher, A. Benisek, W. Sitte, W. Preis, I. Rom, F. Hofer**  
 "Transport properties of  $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-d}$ ", Solid State Ionics 141-142 (2001) 375-380.
- A. Schröder, W. Sitte, I. Rom, G. Kothleitner, F. Hofer**  
 "Formation of interfacial nano-layers in the system Pt-Ni-O", Solid State Ionics 141-142 (2001) 177-183.
- A. Schröder, W. Sitte, I. Rom, W. Grogger, F. Hofer**  
 "Interfacial pattern formation in the Pt-Ni-O system studied by energy-filtering transmission electron microscopy", Defect and Diffusion Forum Vols. 194-199 (2001) 1563-1568.
- F. Hofer, J. Mayer, H. Kohl**  
 „Berichte aus den DGE-Arbeitskreisen: Energiefilterung und Elektronenenergieverlustspektroskopie (EELS-EFTM)", Elektronenmikroskopie 21 (2001) 36-37.
- P. Golob, F. Hofer, P. Wilhelm**  
 „Seit 50 Jahren Partner der Industrie - Das Zentrum für Elektronenmikroskopie Graz“, Gießerei-Praxis 8 (2001) 319-323.
- S. Däbritz, H. Horn, H. Waltinger**  
 "Detection of crystal lattice defects in microranges of copper by X-ray interferences", J. Anal. At. Spectrom. 14 (2001) 487-492.
- P. Feiertag, T. Kavc, U. Meyer, I. Gsoels, W. Kern, I. Rom, F. Hofer**

- “Patterned modification of polymer surfaces employing UV sensitive gases”, *Synthetic Metals* 121 (2001) 1371-1372.
- I. Rom, M. Wachtler, I. Papst, M. Schmied, J. O. Besenhard, F. Hofer, M. Winter**  
 “Electron microscopical characterization of Sn/SnSb composite electrodes for lithium-ion batteries”, *Solid State Ionics* 143 (2001) 329-336.
- H. Buqa, P. Golob, M. Winter, J. O. Besenhard**  
 “Modified carbons for improved anodes in lithium ion cells”, *J. of Power Sources* 97-98 (2001) 122-125.
- F. Hofer, P. Warbichler, H. Kronberger, J. Zweck**  
 “Mapping the chemistry in nanostructured materials by energy-filtering transmission electron microscopy (EFTEM)”, *Spectrochimica Acta Part A* 57 (2001) 2061-2069.
- W. Grogger, F. Hofer, P. Warbichler, G. Kothleitner**  
 “Quantitative Energy-filtering Transmission Electron Microscopy in Materials Science”, *Microscopy and Microanalysis* 6 (2001) 161-172.
- C. Angelkort, H. Lewalter, P. Warbichler, F. Hofer, W. Bock, B. O. Kolbesen**  
 “Formation of niobium nitride by rapid thermal processing”, *Spectrochimica Acta Part A* 57 (2001) 2077-2089.
- F. Hofer, P. Warbichler, A. Scott, R. Brydson, I. Galesic, B. Kolbesen**  
 “Electron energy loss near edge structure on the nitrogen K-edge in vanadium nitrides”, *Journal of Microscopy* 204 (2001) 166-171.
- P. Warbichler, F. Hofer, W. Grogger, A. Lackner**  
 “EFTEM-EELS Characterization of VC and Cr<sub>3</sub>C<sub>2</sub> Doped Cemented Carbides”, 15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer & H. Wildner, Vol. 2 (2001) 65-74.
- P. Hofer, H. Cerjak, P. Warbichler**  
 “Quantification of precipitates in a 10%Cr steel using TEM and EFTEM”, *Materials Science and Technology* 16 (2001) 1221-1225.
- G. Wirnsberger, K. Gatterer, H. P. Fritzer, W. Grogger, B. Pillep, P. Behrens, M. F. Hansen, C. Bender Koch**  
 “Mesostructured Iron Oxyhydroxides. 1. Synthesis, Local Structure, and Magnetism”, *Chemistry of Materials* 13 (2001) 1453-1466.
- G. Wirnsberger, K. Gatterer, H. P. Fritzer, W. Grogger, B. Pillep, P. Behrens, M. F. Hansen, C. Bender Koch**  
 “Mesostructured Iron Oxyhydroxides. 2. Soft Hydrothermal Restructuring Processes”, *Chemistry of Materials* 13 (2001) 1467-1472.
- E. Letofsky, H. Cerjak, I. Papst, P. Warbichler**  
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**I. Papst, G. Kothleitner, F. Hofer, L. Binder**

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## 2002

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**M. Schmied, P. Pölt**

“Particle analysis by SEM/EDXS and specimen damage”, *Mikrochim. Acta* 139 (2002) 171-177.

**E. Kozeschnik, P. Pölt, S. Brett, B. Buchmayr**

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**W. Fischer, M. Schiller, P. Wilhelm, A. Gupper**

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**G. Gärtner, E. Ingolic**

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“Morphology of a PA/PTFE Blend Studied by Raman Imaging”, *Macromol. Symp.* 184, (2002) 275-285.

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“Electrolyte Interactions with Graphite Anodes Exhibiting Structures with Various Amounts of Rhombohedral Phase”, *IMLB 11*, Monterey CA, USA. (2002) pp.??

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**A. Gupper, P. Wilhelm**

„Mikro-Raman Spektroskopie: Eine exzellente Methode zur Bestimmung von Orientierung und Kristallinität in Polymeren“, 52. Jahrestagung der Österreichischen Physikalischen Gesellschaft, Leoben, (2002) S. 45.

**A. Gupper, P. Wilhelm, M. Schiller**

“Degradation of poly (vinyl chloride) with Different Additives Studied by Micro Raman Spectroscopy”, *FACSS 2002*, Providence (USA), Book of Abstracts, (2002) p. 142.

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“Molecular Orientation and Crystallinity of some Commercial Polypropylene Products studied by Micro Raman Spectroscopy”, *FACSS 2002*, Providence (USA), Book of Abstracts, (2002) p. 173.

**A. Gupper, P. Wilhelm, M. Schiller**

“Degradation of poly (vinyl chloride) with Different Additives Studied by Micro Raman Spectroscopy”, *Addcon World 2002*, Budapest, Conference Proceedings, (2002) pp. 227-235.

**A. Gupper, P. Wilhelm, M. Schmied, S. G. Kazarian, A. K. L. Chan, J. Reußner**

“Imaging Methods for Morphological Investigations on a Polymer Blend”, 10. Österreichische Chemietage, Linz, Wissenschaftliche Beiträge, (2002) PO-33.

**W. Grogger, K. M. Krishnan, F. Hofer**

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 „Chemische Bindungsinformation aus nanometergrossen Probenbereichen mittels eines neuartigen analytischen Transmissionselektronenmikroskops“, 10. Österreichische Chemietage, Linz, Wissenschaftliche Beiträge (2002) PO-21.
- J. Engstler, J. J. Schneider, B. Günther, F. Kaldasch, G. Müller, C. Mitterbauer, F. Hofer**  
 “A Single Source Strategy to Aligned Isolated Carbon Nanotubes”, 10. Österreichische Chemietage, Linz, Wissenschaftliche Beiträge (2002) PO-90.
- B. Schaffer, W. Grogger, F. Hofer**  
 „Abbildung ultradünner Siliziumoxidschichten in Halbleiterbauelementen mittels energiegefilterter Elektronenmikroskopie“, 52. Jahrestagung der Österreichischen Physikalischen Gesellschaft, Leoben (2002) S. 75.
- M. Dietzel, I. Letofsky-Papst**  
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- S. Lipovšek, I. Letofsky-Papst, F. Hofer, M.A. Pabst**  
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- W. Sitte, E. Bucher, W. Preis, I. Papst, W. Grogger, F. Hofer**  
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 “Methanol crossover suppression in direct methanol fuel cells by sub-micron palladium layers”, *Advanced Batteries and Accumulators - 3<sup>rd</sup> International Conference, Brno, Abstracts* (2002) p. 15/1-15/3.
- F. Hofer, P. Warbichler, I. Letofsky-Papst**  
 „Nanoanalytik von Sekundärphasen in Stählen mittels Energie Filterung im Durchstrahlungselektronenmikroskop“, *Berg- und Hüttenmännische Monatshefte*, 147(9), (2002) 263-267.
- G. Angeli, H. Deinhammer, J. Faderl, I. Papst, M. Wolpers**  
 “Distribution and composition of surface oxides on high strength IF-steel after recrystallisation annealing”, *44th Mechanical Working and Steel Processing Conference Proceedings, 8th International Rolling Conference and International Symposium on Zinc-Coated Steels, Vol. XL*, (2002) p. 825.
- M. Gahleitner, A. Hauer, K. Bernreitner, E. Ingolic**  
 “Polypropylene-based Model Compounds as Tools for the Development of High-impact-ethylene-propylene Copolymers”, *Intern. Polym. Proc*, Vol. VII (4), (2002) 1-7.

## 11. Oral Presentations by Members of the Institute Vorträge von Institutsmitarbeitern

### 2001

#### **F. Hofer** (invited)

„Compositional mapping with EFTEM and its future“,  
Symposium on “Future Perspectives of Transmission Electron Microscopy in Materials  
Science”; Max-Planck Institut für Metallforschung, Stuttgart, BRD, January 18 and 19, 2001.

#### **G. Kothleitner**

„Prospects and Limitations of EFTEM“, BRITE EURAM-Meeting, Eindhoven, NL, January 28  
to 30, 2001.

#### **G. Kothleitner** (invited)

„Energy-filtering TEM: Performance limiting factors with respect to different modes of  
operation“, AMAS VI – The Sixth Biennial Symposium SPM III – The Third Scanned Probe  
Microscopy Conference, Sidney, Australia, February 8 to 20, 2001

#### **F. Hofer**

„Nanoanalyse im Elektronenmikroskop“, SFB-Workshop on Nanoscale Composites:  
Synthesis, Characterization, Reactivity and Properties of Materials with Inner Surfaces, Karl-  
Franzens-Universität Graz, February 20 and 21, 2001.

#### **F. Hofer** (invited)

„Quantitative compositional imaging with energy-filtering TEM“  
Eur. Conf. Geosciences, Straßburg, France, April 8 to 12, 2001.

#### **W. Grogger**

„New approaches for the characterization of hard materials by analytical electron  
microscopy“, 15<sup>th</sup> Int. PLANSEE-Seminar, May 28 to June 1, 2001.

#### **C. Mitterbauer**

„ELNES investigation of Ti-oxides“, PICS-Meeting, Vienna University of Technology, June 28  
and 29, 2001.

#### **G. Kothleitner** (invited)

„Applications and performance limiting factors in different modes of operation“, EFTEM-  
Meeting, Oxford, UK, July 7, 2001.

#### **F. Hofer** (invited)

„Compositional Mapping with Energy Filtering TEM: The Present Status“, Microscopy &  
Microanalysis Conference, Long Beach, California, August 5 to 9, 2001.

#### **G. Kothleitner**

„Difference Spectrum Images: Numerical Filters Applied to EELS 3D Data Sets“, Microscopy  
& Microanalysis Conference, Long Beach, California, August 5 to 9, 2001.

#### **P. Pölt**

„Automated Analysis of Submicron Particles by CCSEM/EDXS – Where are the limits“,  
EMAG 2001, Dundee, UK, September 4 to 9, 2001.

**F. Hofer** (invited)

„High Resolution Analytic Methods“, Dreiländertagung für Elektronenmikroskopie, Innsbruck, September 9 to 14, 2001.

**M. Schmied**

„Submicron Particle Analysis by SEM / EDXS – Quantitative Accuracy and Specimen Damage“, Dreiländertagung für Elektronenmikroskopie, Innsbruck, September 9 to 14, 2001.

**I. Letofsky-Papst**

„Microstructure of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  investigated by EELS, EFTEM and HRTEM“, Dreiländertagung für Elektronenmikroskopie, Innsbruck, September 9 to 14, 2001.

**C. Mitterbauer**

“Electron energy-loss near-edge fine structure investigations of titanium oxides“, Dreiländertagung für Elektronenmikroskopie, Innsbruck, September 9 to 14, 2001.

**A. Gupper**

“Quantitative micro Raman spectroscopy for in-situ-studies on the thermal degradation of PVC“, 5<sup>th</sup> Austrian Polymer Meeting, Leoben, September 9 to 14, 2001.

**G. Kothleitner** (invited)

„Energy Filtering TEM: The Present Status“, 40. Annual Conference of the Microscopy Society of Southern Africa, Johannesburg, South-Africa, November 28 to December 7, 2001.

**2002****F. Hofer**

„Moderne Analytische Elektronenmikroskopie“, Hauptversammlung der Österr. Gesellschaft f. Elektronenmikroskopie, Wien, January 30, 2002.

**F. Hofer**

„Nanoanalytical characterization of Steels and Alloys“, COST-Tagung, Graz, February 28, 2002.

**F. Hofer**

„EFTEM-EELS: New results from the TU Graz“, FEG-Usermeeting, FEI Eindhoven, NL, March 5 and 6, 2002.

**F. Hofer**

„Nanobereichsanalytik mittels energiefilternder Transmissionselektronenmikroskopie (Grundlagen und Anwendungen in den Materialwissenschaften)“, Vienna University of Technology, March 15, 2002.

**G. Kothleitner** (invited)

„Introduction to Energy-Filtering Transmission Electron Microscopy“ and „Towards Quantitative EELS Mapping“, EELS-EFTEM-School at Gatan, Pleasanton, USA, April 15 to 19, 2002.

**W. Grogger**

“Spatial Resolution and Detection Limits in EFTEM“, SALSA 2002, Guadeloupe, May 5 to 9, 2002.

**G. Kothleitner**

“Elemental Occurrence Maps: A Starting Point for Quantitative EELS Spectrum Image Processing”, SALSA 2002, Guadeloupe, May 5 to 9, 2002.

**F. Hofer**

„Neue Entwicklungen und Trends in der Energiefilterungs-Transmissions-elektronenmikroskopie“, Symposium “Professor Reimer”, Universität Münster, BRD, May 29, 2002.

**W. Grogger**

„Chemical Analysis on a Nanometer Length Scale by Energy-Filtering TEM: Principles and Practical Applications“, 9<sup>th</sup> Joint Vacuum Conference, Seggau, June 16 to 20, 2002.

**F. Hofer** (invited)

„Quantitative EELS and EFTEM“, Annual BRITE EURAM-Meeting 2002, Delft, NL, June 24 and 25, 2002.

**F. Hofer** (invited)

"Impact of new nanoanalytical techniques on the development of materials", Festveranstaltung “Forum für Metallurgie und Werkstoffe 2002” of the Austrian Society for Metallurgy and Materials, Linz, June 27, 2002.

**W. Grogger** (invited)

„EFTEM at High Magnification: Principles and Practical Applications“, Microscopy & Microanalysis Conference, Quebec City, Canada, August 4 to 8, 2002.

**G. Kothleitner**

„Comparative ELNES Measurements on Selected Transition Metal Oxides on a New High Energy-Resolution Spectrometer/Monochromator TEM“, Microscopy & Microanalysis Conference, Quebec City, Canada, August 4 to 8, 2002.

**P. Wilhelm**

„Micro Raman Spectroscopy: An Appropriate Method for the Characterization of Orientation and Crystallinity of Polypropylene“, Microscopy & Microanalysis Conference, Quebec City, Canada, August 4 to 8, 2002.

**A. Gupper**

“Degradation of Poly-(Vinyl-Chloride)-studies by Micro Raman Spectroscopy“, XVIIIth International Conference on Raman Spectroscopy, Budapest, Hungary, August 25 to 30, 2002.

**C. Mitterbauer**

„High energy resolution EELS using a monochromized 200 kV TEM: Comparative investigation of the Ti L<sub>2,3</sub> edge of rutile (TiO<sub>2</sub>)“, 15<sup>th</sup> Int. Congress on Electron Microscopy, Durban, South-Africa, September 1 to 6, 2002.

**I. Letofsky-Papst**

„Charakterisierung von Ausscheidungen in Cr-Stählen mittels EELS und EFTEM“, Metallographie-Tagung, Leoben, September 11 to 13, 2002.

**P. Wilhelm**

„Imaging Methodes for Morphological Investigations on a Polymer Blend“, 10. Österr. Chemietage, Linz, September 17 to 19, 2002.

**A. Gupper**

„Mikro-Raman Spektroskopie: eine exzellente Methode zur Bestimmung von Orientierung und Kristallinität in Polymeren“, ÖPG-Tagung, Leoben, September 23 to 26, 2002.

**F. Hofer** (invited)

„Kantenfeinstrukturen und Anwendungen des Monochromator TEMs“, Arbeitskreistreffen EF-EELS, Max-Planck-Institut für Metallforschung, Stuttgart, BRD, September 24 to 27, 2002.

**G. Kothleitner** (invited)

„Quantitative Analyse in EELS und EFTEM“, Arbeitskreistreffen EF-EELS, Max-Planck-Institut für Metallforschung, Stuttgart, BRD, September 24 to 27, 2002.

**C. Mitterbauer**

„Comparative electron energy-loss near-edge fine structure investigations of titanium oxides“, Arbeitskreistreffen EF-EELS, Max-Planck-Institut für Metallforschung, Stuttgart, BRD, September 24 to 27, 2002.

**W. Grogger**

„Imaging of Ultrathin SiO<sub>2</sub> Layers by using Low-Loss EFTEM“, Arbeitskreistreffen EF-EELS, Max-Planck-Institut für Metallforschung, Stuttgart, BRD, September 24 to 27, 2002.

**I. Letofsky-Papst** (invited)

„Micro-Characterization of Precipitates in 9-12% Cr-Steels using EELS and EFTEM“, Materials Week, München, BRD, September 30 to October 2, 2002.

**A. Gupper**

„Molecular Orientation and Crystallinity of some Commercial Polypropylene Products studies by Micro Raman Spectroscopy“, 29<sup>th</sup> Annual Meeting: Federation of Analytical Chemistry and Spectroscopic Societies, Providence, USA, October 13 to 17, 2002.

**A. Gupper**

„Degradation of poly (vinyl chloride) with different additives studied by micro Raman spectroscopy“, 8<sup>th</sup> International Plastics Additives and Modifiers Conference, Budapest, Hungary, October 22 and 23, 2002.

**P. Pölt** (invited)

„Materialcharakterisierung im REM – topografisch, chemisch und kristallografisch“, Symposium „Oberflächencharakterisierung“ PROFACTOR, Steyr, October 23, 2002.

**F. Hofer**

„Application Results with the new 3D Infinite Focus Microscope“, Alicona-User-Meeting, Grambach/Graz, October 24, 2002.

**G. Kothleitner** (invited)

„EELS spectroscopy and imaging: applications on new spectrometers“, Joint Meeting 2002 of JEM-users, Halle, BRD, October 29, 2002.

**F. Hofer** (invited)

„Nanoanalytik mittels Energiefilterung im Durchstrahlungselektronenmikroskop“, Nanoforum, University of Linz, November 15, 2002.

**F. Hofer**

„Einsatz der Hochauflösungselektronenmikroskopie in der modernen Materialforschung“, Omya, Oftringen, Switzerland, November 25, 2002.

**P. Pölt**

"Einsatz der Rasterelektronenmikroskopie in der modernen Materialforschung", Omya, Oftringen, Switzerland, November 25, 2002.

**G. Kothleitner** (invited)

"Performance tests and measurements on selected transition metal oxides with a new high-resolution EELS spectrometer", PICS-Programm "Challenge in ELNES", Paris, France, November 25 to 27, 2002.

**F. Hofer**

„High resolution EELS with a new monochromized TEM applied to nanoscale structure studies“, Material Research Society Conference, Boston, USA, December 2 to 6, 2002.

**F. Hofer**

"Nanocharakterisierung von Festkörpern mittels Energiefilterungs-Transmissions-elektronenmikroskopie", Technical University of Berlin, BRD, December 17 and 18, 2002.



The newly renovated secretariat of the institute

## 12. Poster Presentations by Members of the Institute Posterpräsentationen von Institutsmitarbeitern

2001

**P. Pölt and M. Schmied**

„Particle Analysis by SEM/EDXS and Specimen Damage“, 7th European Workshop on Modern Developments and Applications in Microbeam Analysis, Tampere, Finland, May 6 to 10, 2001

**P. Wilhelm**

„Morphology of a PA/PTFE Polymer Blend Studied by Raman Imaging“, 1<sup>st</sup> International Conference on Advanced Vibrational Spectroscopy, Turku, Finland, August 18 to 26, 2001.

**A. Gupper**

„Crystallinity and Orientation of Highly Oriented PP-Fibres Studied by Micro Raman Spectroscopy“, 1<sup>st</sup> International Conference on Advanced Vibrational Spectroscopy, Turku, Finland, August 18 to 26, 2001.

**P. Wilhelm**

„Morphology of a PA/PTFE Polymer Blend Studied by Raman Imaging“, 14<sup>th</sup> European Symposium on Polymer Spectroscopy, Dresden, BRD, September 1 to 6, 2001.

**A. Gupper**

„Crystallinity and Orientation of Highly Oriented PP-Fibres Studied by Micro Raman Spectroscopy“, 14<sup>th</sup> European Symposium on Polymer Spectroscopy, Dresden, BRD, September 1 to 6, 2001.

**S. Mitsche**

„Automated Analysis of Submicron Particles by CCSEM - What is the real particle size?“, Dreiländertagung für Elektronenmikroskopie, Innsbruck, September 9 to 14, 2001.

**G. Kothleitner**

„Digital filters applied to EELS spectrum images“, Dreiländertagung für Elektronenmikroskopie, Innsbruck, September 9 to 14, 2001.

**B. Brunegger**

„Non-centric ion milling: a method to achieve better thinning results in TEM specimen preparation“, Dreiländertagung für Elektronenmikroskopie, Innsbruck, September 9 to 14, 2001.

**P. Wilhelm**

„Morphology of a PA/PTFE polymer blend studied by micro Raman spectroscopy“, 5<sup>th</sup> Austrian Polymer Meeting, Leoben, September 12 to 14, 2001.

**A. Gupper**

„Crystallinity and Orientation of highly oriented PP-fibres studied by micro Raman spectroscopy“, 5<sup>th</sup> Austrian Polymer Meeting, Leoben, September 12 to 14, 2001.

**A. Gupper**

„Raman and FTIR investigations on a commercial PA/PTFE blend“, Vibrational Spectroscopy in Colloid & Interface Science, Oxford, UK, September 17 to 20, 2001.

## **2002**

### **F. Hofer**

“Pushing EELS energy resolution: ELNES studies on transition metal oxides”, SALSA 2002, Guadeloupe, May 5 to 9, 2002.

### **A. Gupper and P. Wilhelm**

„Raman Imaging and Confocal Laser Scanning Microscopy for Polymer Blend Characterization“, Symposium on Optical-Spectroscopic Imaging, Dresden, BRD, June 14, 2002.

### **I. Letofsky-Papst**

„AEM Investigation of Strontium Substituted La-Co-Perovskites“, Microscopy & Microanalysis, Quebec City, Canada, August 4 to 8, 2002.

### **A. Gupper**

„Raman Microscopic Studies on the Orientation and Crystallinity of Polypropylene“, XVIIIth International Conference on Raman Spectroscopy, Budapest, Hungary, August 25 to 30, 2002.

### **P. Wilhelm**

„Investigations on the Morphology of a Commercial PA/PTFE Blend: A Comparison of different Analytical Methods for Polymer Characterization“, XVIIIth International Conference on Raman Spectroscopy, Budapest, Hungary, August 25 to 30, 2002.

### **C. Mitterbauer**

„ELNES as a fingerprint for identifying chromium nitrides“, 15<sup>th</sup> Int. Congress on Electron Microscopy, Durban, South-Africa, September 1 to 6, 2002.

### **S. Mitsche**

„SEM, submicron particles – and the real particle size?“, 15<sup>th</sup> Int. Congress on Electron Microscopy, Durban, South-Africa, September 1 to 6, 2002.

### **P. Pöit**

„EBSD-Contamination, specimen damage, tilt and pattern quality“, 15<sup>th</sup> Int. Congress on Electron Microscopy, Durban, South-Africa, September 1 to 6, 2002.

### **M. Schmied**

„Radiation damage of inorganic substances in SEM and TEM“, 15<sup>th</sup> Int. Congress on Electron Microscopy, Durban, South-Africa, September 1 to 6, 2002.

### **C. Mitterbauer**

„Chemische Bindungsinformation aus nanometergroßen Probenbereichen mittels eines neuartigen analytischen Transmissionselektronenmikroskops“, 10. Österr. Chemietage, Linz, September 17 to 19, 2002.

### **P. Wilhelm**

“Imaging Methods for Morphological Investigations on a Polymer Blend”, 10. Österr. Chemietage, Linz, September 17 to 19, 2002.

### **B. Schaffer**

„Abbildung dünner Siliziumoxidschichten im Nanometerbereich mittels energiegefilterter Transmissionselektronenmikroskopie“, ÖPG-Tagung, Leoben, September 23 to 26, 2002.

### **A. Gupper**

„Degradation of poly (vinyl chloride) with different additives studied by micro Raman spectroscopy“ (Award Certificate!), 29<sup>th</sup> Annual Meeting: Federation of Analytical Chemistry and Spectroscopic Societies), Providence, USA, October 13 to 17, 2002.

## **13. Research Visits of Staff Members in other Institutions / Forschungsaufenthalte von Institutsmitarbeitern**

- September 1999 – February 2001: Dipl.-Ing. Dr. Werner Grogger at the National Center for Electron Microscopy of the Lawrence Berkeley Laboratory in Berkeley, USA  
Work plan: “Energy-filtering TEM at high spatial resolution”
- May 2001: Dipl.-Ing. Mario Schmied at VTT, Espoo (Finland):  
Work plan “Automated analysis of Submicron Particles by SEM/EDXS”
- June 2001: Dipl.-Ing. Andreas Gupper at Instituto de Ciencia de Materiales, Sevilla (Spain):  
Work plan: “Characterization of nanostructured coatings by XPS and Raman spectrometry”
- Nov. 2001: Dipl.-Ing. Christoph Mitterbauer at University of Leeds, Leeds (U.K.):  
Work plan “Simulation of EELS near edge fine structures”
- Nov. 2001: Dipl.-Ing. Dr. Ilse Papst at EMAT, University of Antwerpen (Belgium):  
Work plan “ Electron diffraction of perowskites”

## **14. Scientific Co-operations / Wissenschaftliche Zusammenarbeit**

### **Technische Universität Graz / Graz University of Technology:**

Institut für Werkstoffkunde, Festigkeitslehre und Materialprüfung  
 Institut für Materialprüfung und Baustofftechnologie  
 Institut für Verbrennungskraftmaschinen und Thermodynamik  
 Institut für Papier-, Zellstoff- und Fasertechnik  
 Institut für Grundlagen der Verfahrenstechnik und Anlagentechnik  
 Institut für Elektrische Anlagen und Hochspannungstechnik  
 Institut für Technische Geologie und Angewandte Mineralogie  
 Institut für Physikalische u. Theoretische Chemie  
 Institut für Chemische Technologie organischer Stoffe  
 Institut für Chemische Technologie anorganischer Stoffe  
 Institut für Biochemie  
 Institut für Lebensmittelchemie- und Technologie  
 Institut für Mineralogie  
 Institut für Festkörperphysik  
 Institut für Experimentalphysik  
 Institut für Technische Physik  
 Institut für Mikrobiologie und Abfalltechnologie

### **Universität Graz / University of Graz:**

Institut für Histologie und Embryologie  
 Institut für Chemie  
 Institut für Experimentelle Pathologie  
 Institut für Zoologie

Institut für medizinische Biochemie  
Institut für Pflanzenphysiologie

**Montanuniversität Leoben / University of Leoben:**

Institut für Analytische Chemie  
Institut für Physikalische Chemie  
Institut für Metallphysik  
Institut für Physik  
Institut für Metallkunde und Werkstoffprüfung

**Technische Universität Wien / Vienna University of Technology:**

Institut für Angewandte u. Technische Physik  
Institut für Materialchemie  
Institut für Chemische Technologie anorganischer Stoffe  
Institut für Analytische Chemie

**Universität Wien / University of Vienna:**

**Universität Innsbruck / University of Innsbruck:**

Institut für Botanik

**Joanneum Research, Graz**

Institut für Nanostrukturierte Materialien und Photonik

**Österreichische Akademie der Wissenschaften / Austrian Academy of Sciences:**

Erich Schmid Institut Leoben

**Österr. Gießerei Institut Leoben / Austrian Foundry Research Institute, Leoben**

**Johann Wolfgang Goethe Universität Frankfurt am Main, BRD**

Institut für Anorganische und Analytische Chemie

**University of Ljubljana, Slovenia**

Department for Textiles

Department of Biology

**Delft University of Technology, The Netherlands**

Laboratory of Materials Science

**VTT Processes, Espoo, Finland**

**Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, BRD**

Abteilung für Anorganische Chemie

**Instituto de Ciencia de Materiales, Sevilla, Spain**

**National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory, Berkeley, USA**

## 15. Abstracts of Scientific Main Results 2001-2002 Kurzbeschreibungen wichtiger Ergebnisse 2001-2002

With the next pages we try to give an impression of the very many activities that have characterized our research during the last two years. Some contributions have been included in revised form from conference proceedings, others have been extracted from already published papers in scientific journals.

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## Radiation Damage of Inorganic Substances in SEM and TEM

M. Schmied, P. Pölt, F. Hofer

Research Institute for Electron Microscopy, Graz University of Technology, Austria

Radiation damage of both organic and inorganic materials can be frequently observed in electron microscopy. These effects have been addressed for many years by various scientists<sup>1,2</sup> with special focus on high electron energies in TEM, mainly for biological samples and polymers. In SEM, radiation damage, apart from alkaline diffusion, often seems to be regarded as a minor side effect. It has generally been neglected for most inorganic substances. Additionally, much less attention has been devoted to the influence of radiation damage on the quantitative EDXS analysis of inorganic substances, especially also in particle analysis of environmental samples.

A detailed investigation<sup>3</sup> of radiation damage in SEM on inorganic solids (e.g. potassium sulphate) proved, that, as has been also stated by Reimer<sup>1</sup>, the amount of damage increases with an increasing electron dose. In the case of potassium sulphate a total decomposition of the particles, with a total loss of sulphur, could be observed at an acceleration voltage of 7 keV and a probe current of 0.7 nA (Fig.1). Just a bright blot remains, which is larger in size than the original particle itself. An EDXS analysis of the blot (region 1 in Fig.1b) shows, that only potassium and oxygen could be detected. Thus one can suppose, that a kind of potassium oxide has been formed. But specimen damage does also occur for electron energies as low as 1 keV. Similar results have also been observed for a lot of other materials, like ZnCl<sub>2</sub>, KCl, etc.. For particles the amount of damage increases with decreasing particle size, if the electron dose is kept constant.

For an exact determination of the residual oxide TEM investigations on K<sub>2</sub>SO<sub>4</sub> particles have been performed. Figs.2a and 2b clearly show the partial destruction of the particle within 40 sec irradiation time. EELS could confirm the loss of sulphur. Selected area electron diffraction images were recorded at different irradiation times. By rotating the images around their centre, the intensity distribution of the reflexes (rings) could be obtained, and from these reflexes d-values were calculated. Fig.2c demonstrates, that the d-values from the undamaged particle correlate nicely with the d-values from potassium sulphate. For the strongly damaged particle a change in electron diffraction can be observed. Two additional peaks appear, which can be correlated to the d-values of K<sub>2</sub>O, which was previously assumed to be the most probable decomposition remains.

The characterisation of the residuals should give some indications of possible mechanisms responsible for the specimen damage. Especially the combination of SEM and TEM investigations with the wide range of electron energies should yield a better understanding of that kind of "electron-specimen interaction". The facts, that radiation damage appears both at extremely low and high primary electron energies in the same way, and that the amount of damage is dose-dependent, point to specimen melting as one important step in the specimen decomposition.

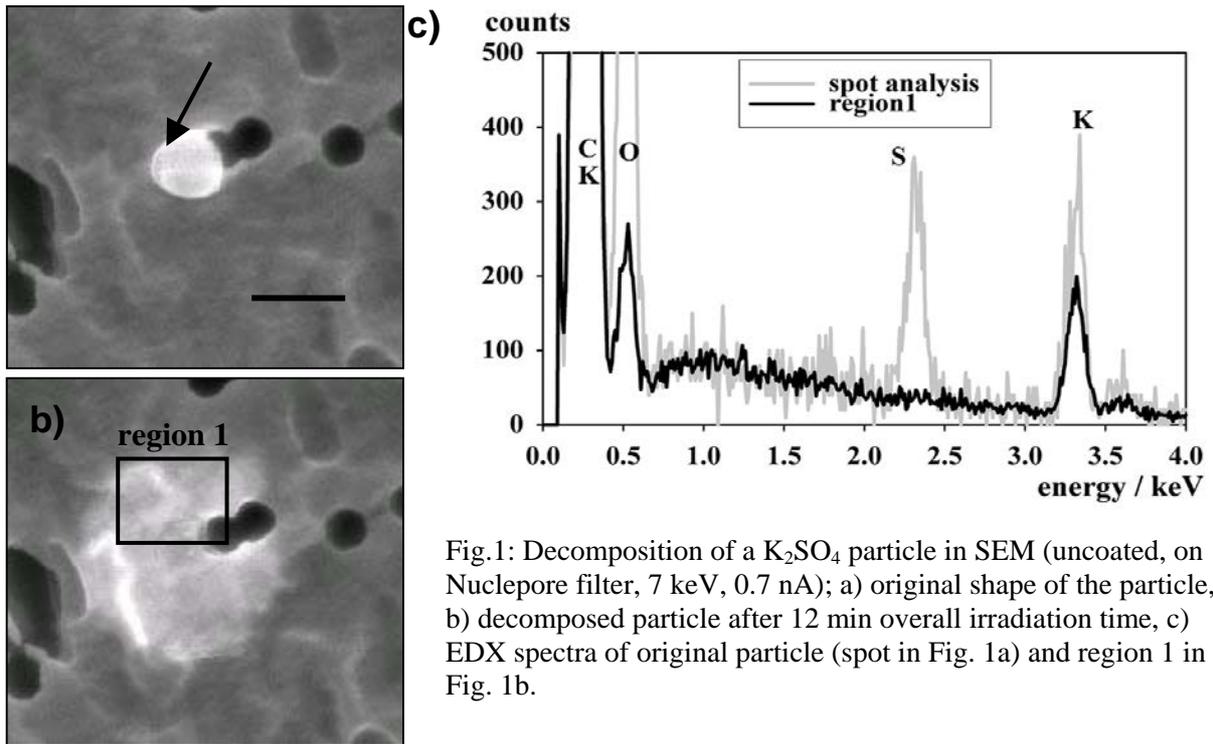


Fig.1: Decomposition of a  $K_2SO_4$  particle in SEM (uncoated, on Nuclepore filter, 7 keV, 0.7 nA); a) original shape of the particle, b) decomposed particle after 12 min overall irradiation time, c) EDX spectra of original particle (spot in Fig. 1a) and region 1 in Fig. 1b.

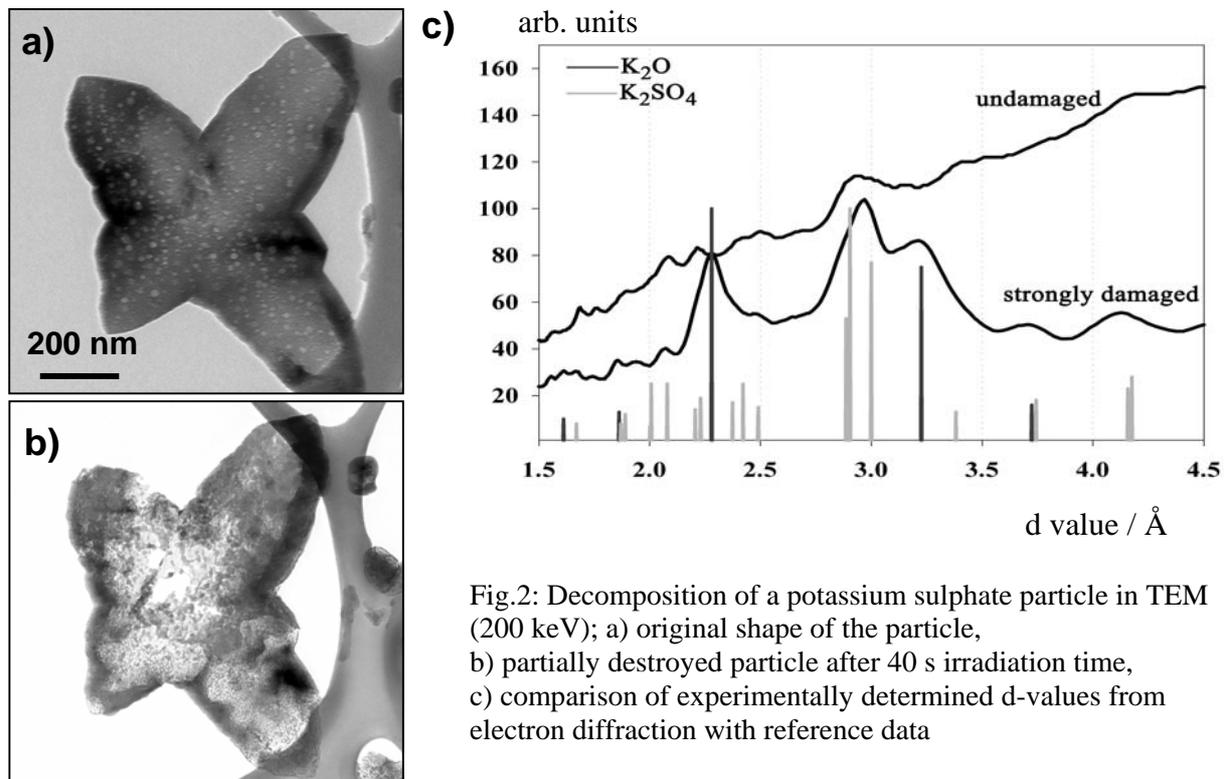


Fig.2: Decomposition of a potassium sulphate particle in TEM (200 keV); a) original shape of the particle, b) partially destroyed particle after 40 s irradiation time, c) comparison of experimentally determined d-values from electron diffraction with reference data

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- [1] L.Reimer, "Scanning Electron Microscopy", Springer (1985) Berlin Heidelberg New York
- [2] L.W. Hobbs, Ultramicroscopy 3 (1979) 381-386.
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## EBSD – Contamination, Specimen Damage, Tilt and Pattern Quality

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The use of EBSD (electron backscatter diffraction) in SEM enables either, if the phase of a sample is known, the determination of its microtexture, or, if its chemistry is known, of its phase. Humphreys demonstrated, that the spatial resolution for Orientation Imaging is mainly dependent on the probe current<sup>1</sup>. Phase analysis is possible for particles even in the submicron region, and the quality of the respective patterns seems to be predominantly dependent on the mounting substrate<sup>2</sup>. But there are also other effects, that can influence resolution and minimum particle size.

Specimen contamination can strongly deteriorate pattern quality. In Fig. 1 IPF (inverse pole figure) maps on a Si – wafer, which was carefully cleaned, are presented. Fig. 1c demonstrates, that the number of wrongly indexed points is much higher in the region, which has been contaminated by a previous scan than on a clean region. The effect would be much more dramatic for a specimen stored for several days on air. In case of strong contamination, resolution would also deteriorate, because the radius of the contamination spots can be much greater than the step size, and thus influence the pattern quality at the following analysis points. Unfortunately, specimen cleaning is not always possible. An example are particles collected on a filter.

A second obstacle, that can deteriorate EBSD – patterns seriously, is radiation damage. Many substances with bad heat conductance, e.g.  $K_2SO_4$ , are extremely prone to radiation damage. In case of particles, there is a strong correlation between the particle size and the amount of damage. The smaller the average diameter of the particle, the shorter the time, until the entire decomposition of the particle is completed<sup>3</sup>. Fig. 2 demonstrates, that in case of a spot analysis on  $K_2SO_4$ , the pattern has nearly faded away after only one minute (compare Figs. 2b and 2c). For submicron particles this may happen even within seconds. A careful investigation of the Duane – Hunt limit of EDX – spectra proved, that this effect is not due to charging and thus a decrease in the primary electron energy. In case of an area analysis, no pattern deterioration can be observed (Fig. 2d). Thus for many types of environmental particles not only full phase analysis, but also a decision, whether the particles are crystalline or amorphous, might be impossible.

But also for supramicron particles an area scan for the recording of an EBSD - pattern is only possible on a flat surface. Otherwise, the tilt of the scan area varies from point to point, and this may cause ‘shading’ (see Fig. 2e). The reason is, that in this case the background differs from point to point, and an optimal correction is impossible. The pattern quality may also be impaired by the fact, that particle surfaces generally are not inclined at a tilt angle of  $70^\circ$ , for which the EBSD – systems are optimised. Already at a change as small as  $5^\circ$  the patterns may become fainter. Generally, the particles of a specimen are single crystals, and since all their surfaces have a different tilt, background correction is always a very difficult task.

We thank the „Forschungsförderungsfonds der gewerblichen Wirtschaft“ (FFF) for supporting this work (Project 803060).

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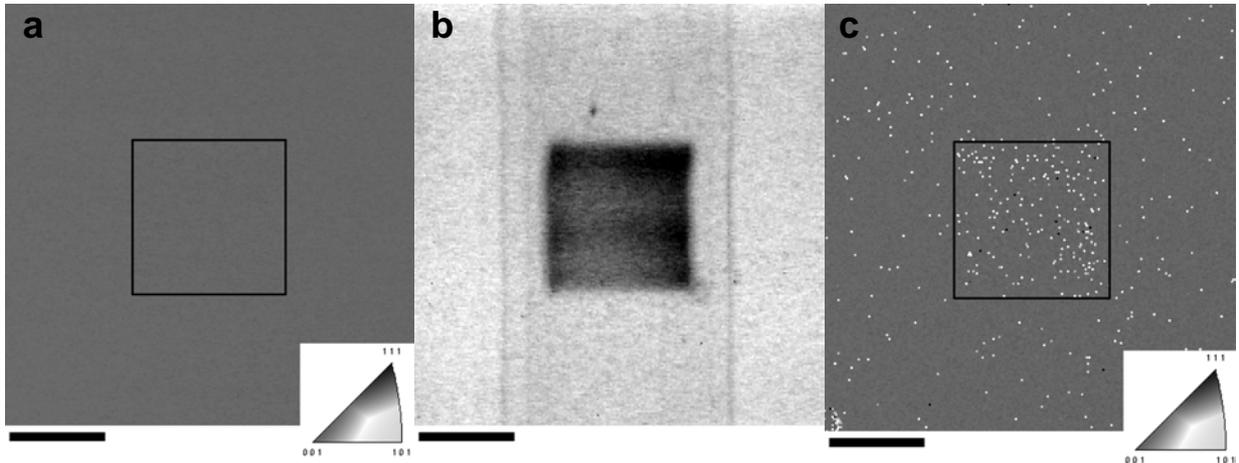


Figure 1. a. IPF – map of an OIM – scan (8 frames, 0.5  $\mu\text{m}$  step size), with a preceding scan at the centre in the marked square (8 frames, 0.17  $\mu\text{m}$  step size); b. The corresponding image quality map; c. IPF – map of a scan subsequently after that of Fig. 1a at the same area (1 frame, 0.5  $\mu\text{m}$  step size); marker length: 20  $\mu\text{m}$ ; Microscope conditions:  $E_0 = 15 \text{ keV}$ ,  $I_p = 2.4 \text{ nA}$ .

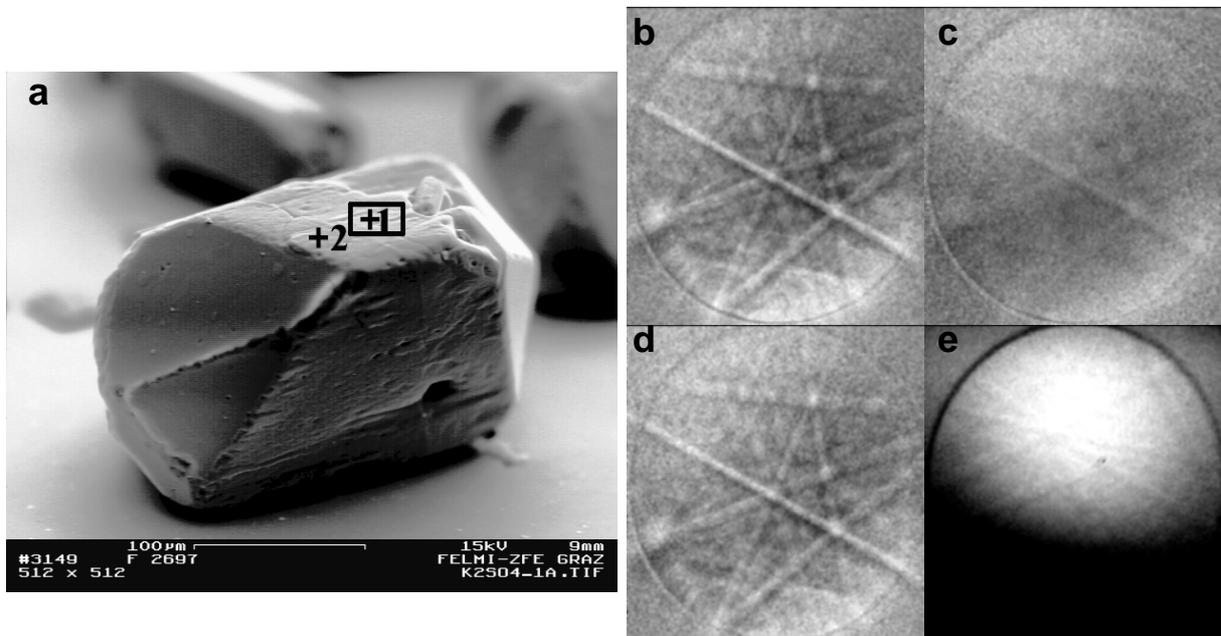


Figure 2. a. SE – image of a  $\text{K}_2\text{SO}_4$  – particle (image width: 370  $\mu\text{m}$ ); b. EBSD – pattern at point 1 immediately after setting the spot; c. EBSD pattern at point 1 after 1 min irradiation at that spot; d. EBSD – pattern after scanning the marked area in Fig. 2a for 5 min; e. EBSD – pattern at point 2, with the same background correction as in Fig. 2b; Microscope conditions:  $E_0 = 15 \text{ keV}$ ,  $I_p = 2.4 \text{ nA}$ .

## SEM, Submicron Particles - and the Real Particle Size?

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The investigation of submicron particles down to a size as low as possible is interesting in many fields of research, e.g. aerosol formation in combustion plants, environmental particles or powder catalysis. Computer controlled SEM (CCSEM) enables the unattended determination of both the geometrical parameters and the chemical composition of thousands of particles. Subsequently a great variety of correlations between all these parameters can be established.

But for particles with a size of a few 100 nm or less, the interaction processes that are responsible for the image formation in SEM, very often have an extension of the size of the particles themselves. As a consequence, the measured particle diameters may strongly differ for different types of detectors. Additionally, a coating, necessary in case of non-conductive particles on a non-conductive substrate, may strongly affect the measured value of the particle size. Vladár has demonstrated, that even contamination can already have a demonstrable effect on the size measurements of submicron particles<sup>1</sup>. Thus, how reliable are these results?

To study the influence of different detectors and coatings on the measured particle size, submicron PbSO<sub>4</sub> – particles have been prepared, dispersed on a Nuclepore filter and coated with either carbon or chromium<sup>2</sup>. The measurements (Fig. 1) demonstrate, that in all cases with the secondary in-lens detector (SI) the greatest particle diameters are measured, whereas the values gained with both the Everhart Thornley detector (SE) and the Backscatter electron detector (BSE) are very similar. The reason may be, that the SI- detector detects mainly SE1 - electrons, and thus is strongest at the edges. On the contrary, for particles with a convex shape, the number of BSE – electrons will decrease from the centre to the boundary, and thus part of the outermost boundary will not be visible in the BSE – image. As the number of the SE2 – electrons is strongly influenced by the number of BSE – electrons, a similar effect may be observed in the SE – image. Additionally, one has to consider, that the interaction volume electrons – specimen is generally much greater than the particles themselves, and therefore also the substrate will influence the measurements. The fact, that the difference between the diameters, measured by the SI – and the other two detectors, increases with decreasing particle size, but is smaller in case of chromium coating compared to carbon coating, fits very well to these explanations. The values for the particle diameters will, of course, also depend on the threshold chosen for the discrimination of the particles from the substrate<sup>3</sup>.

Fig. 2 demonstrates at the example of aerosols sampled at a biomass heating plant, that the results are reproducible down to average particle diameters of 50 nm. That the results are reliable, is proven by Fig. 3, where the automated measurements by CCSEM are compared, although on a rather rough size scale, with the results of the measurements with a 9 stage Berner-type low pressure impactor (BLPI).

Acknowledgement: We thank the Austrian Science Fund (FWF) for sponsoring this work (contract no.: P13527 – TEC).

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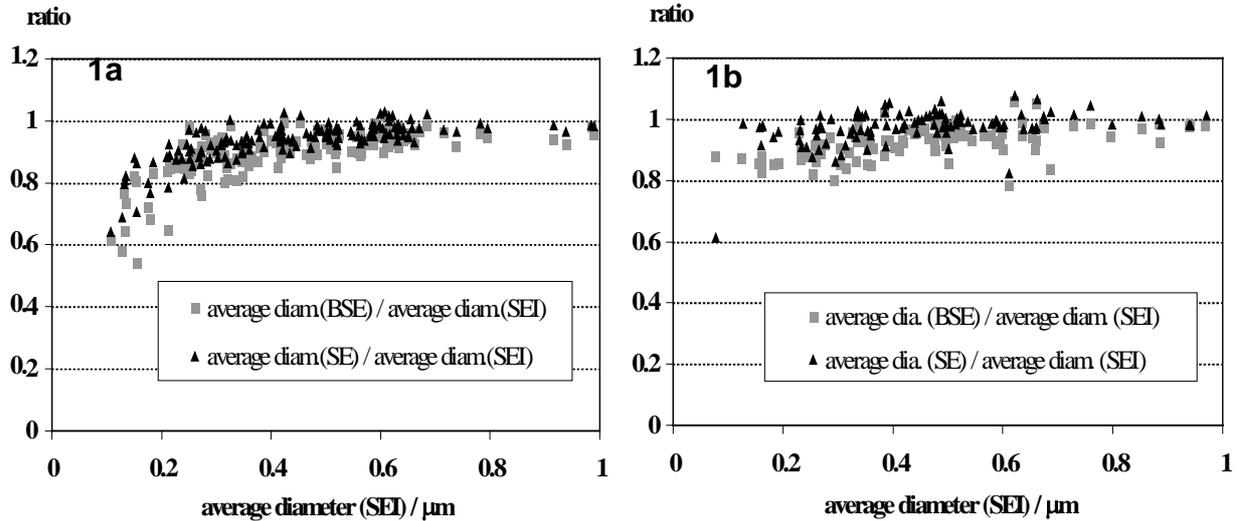


Fig. 1: Comparison of the size of the  $PbSO_4$ - particles, measured with the BSE-, SE- and SI- images ( $E_0=7$  keV). Fig. 1a: particles coated with carbon ( $t=25$  nm). Fig. 1b: particles coated with chromium ( $t=15$  nm).

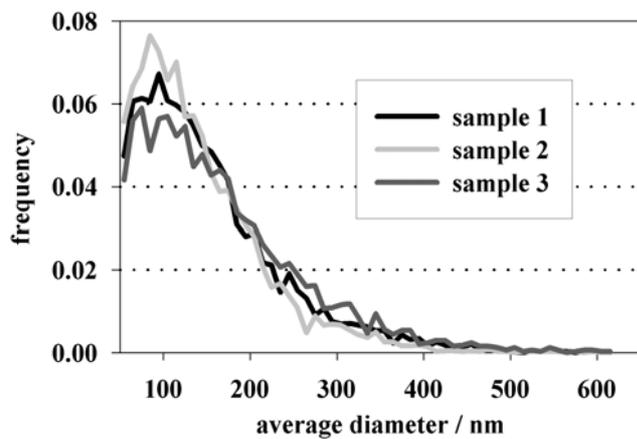


Fig. 2: Dependence of the particle frequency of aerosol-particles on a Nucleopore filter on the average diameter (around 4000 particles per measurement;  $E_0=7$  keV;  $I_p=0.4$  nA).

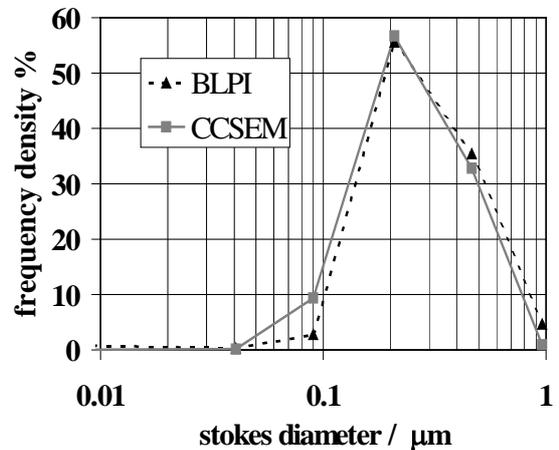


Fig. 3: Dependence of the density distribution of aerosol-particles on the Stokes diameter, measured both by CCSEM and BLPI.

## Measuring the Angular Dependent Energy Distribution of Backscattered Electrons at Variable Geometry

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Many improvements regarding the depth distribution function - the function which describes the place of origin of generated radiation – have been made during the last years. The more information we can get about the shape of the depth distribution function the more accuracy is attained for correction models used in the electron probe microanalysis – in particular pointed to standardless systems. Knowledge of the scattering behaviour of electrons is a highly important component and a critical parameter of the depth distribution functions. Therefore it is not surprising that numerous publications deal with this subject, both theoretically and experimentally. However, little material about investigations of electron scattering at non-vertical electron incidence is available.

An aluminium semi-sphere system with eight detection areas, assembled on a meridian and each covering 0.0026 steradian (Figs. 1 and 2), is put over the solid bulk sample, which is mounted in the eucentric point so that the incident electron beam can be varied in steps of 11.25 degree azimuthally. The complete angular distribution of the backscattered electrons is now available by a polar rotation – in steps of 11.25 degree again - of the semi-sphere. The signals from the detection areas as well as the signal from the rest of the semi-sphere are amplified by operational amplifiers (Burr-Brown OPA128LM, Input Bias Current: max. 75 fA). Additional probe current measurement makes the total amount of electrons accessible. This provides the possibility to normalize the results and compare them with total backscattering coefficients. By the use of opposing voltage (Figs. 3-5) variable up to 10kV inside the detection-assembly it is possible to get an energy resolution of the backscattered electrons at each detection area at the same time.

A comparison of the experimental derived angular-dependent energy distribution at variable angles of incidence with Monte Carlo results [1] is available now. Details of the construction and calibration procedures, possible errors and sources of systematic deviations as well as test results (Fig. 6) are discussed in the doctoral thesis.

The authors gratefully acknowledge the financial support given by the Austrian „Fonds zur Förderung der wissenschaftlichen Forschung“ and „INTAS“.

### References

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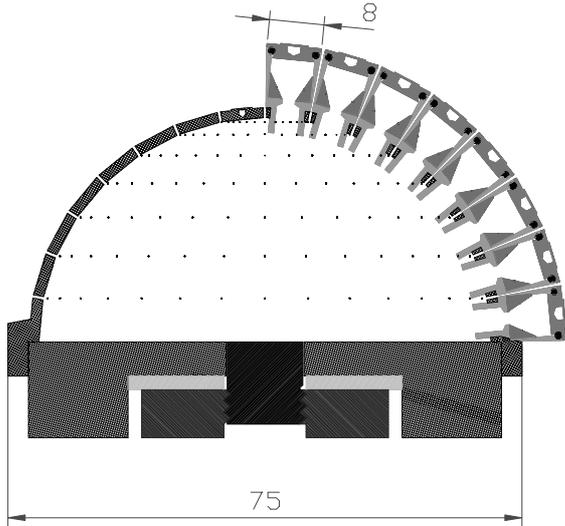


Fig. 1: Schematic view of the detection assembly, distances in mm

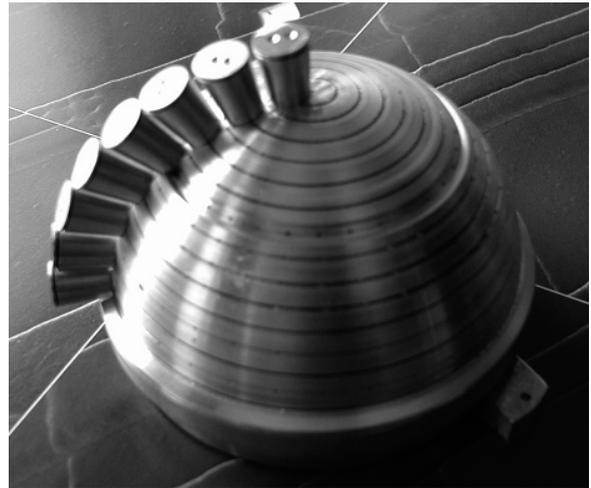


Fig. 2: Image of the semi-sphere with 8 detectors

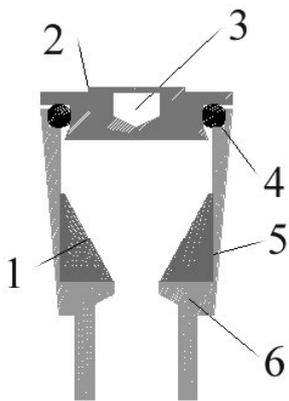


Fig. 3: Schematic view – detecting unit

1 opposing voltage ring, 2 electron receiver, 3 Faraday cup  
4 Insulating ring, 5 insulating Teflon, 6 aluminium envelope

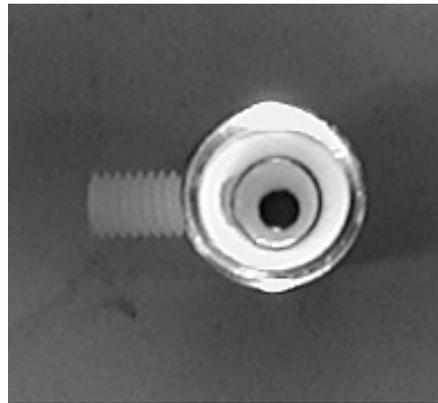


Fig. 4: Top view of an open detector

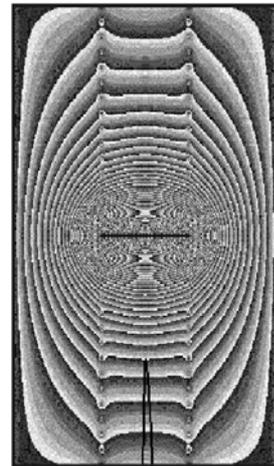


Fig. 5: Simulated electron trajectory

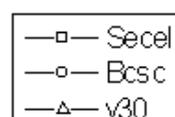
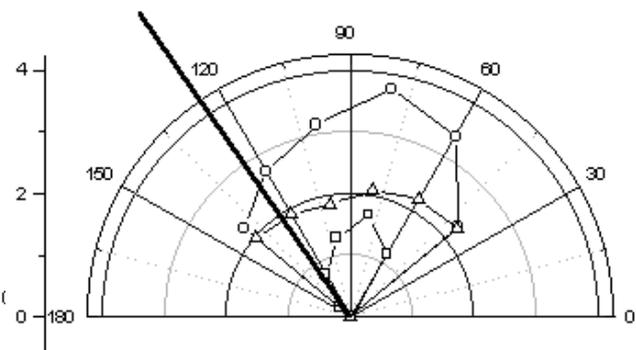
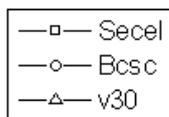
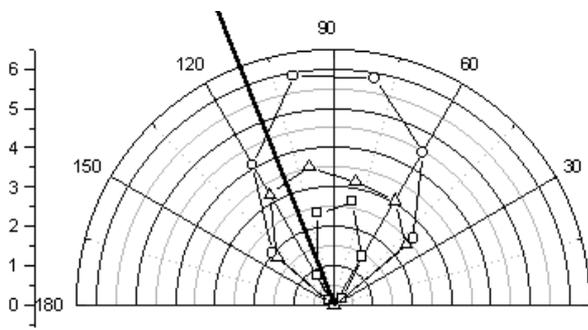


Fig. 6: Prototype testing results for an aluminium bulk sample

## Orientation Imaging Microscopy on 9-12% chromium steels

B. Sonderegger<sup>1</sup>, P. Weinert<sup>1</sup>, P. Pölt<sup>2</sup>, H. Cerjak<sup>1</sup>

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9-12% chromium steels are well established materials for high temperature components in ultra efficient power plants. An important parameter for the usability of the materials is the creep resistance in a temperature range of 550- 650°C for 10<sup>5</sup> hours. Several macroscopic creep models are used to predict the life time of steels. However, a comprehensive prediction of the microstructural evolution of these steels has not been accomplished up to now. Of course such a microstructural model always has to be calibrated on real measurements. With a combination of several measurement techniques an extensive study of the essential microstructural parameters necessary for microstructural modelling is possible, including:

- Size distribution of grains and sub-grains
- Spatial distribution and size distribution of precipitates
- Orientation of sub-grains and precipitates
- Gradients of elemental concentrations in sub-grains and precipitates

For size distributions and spatial distributions of grains, sub-grains and precipitates as well as for the relative misorientation of boundaries the EBSD-method is the most suitable tool.

The orientation of sub-grains and precipitates is measured with a LaB<sub>6</sub> SEM with additional EBSD detector. The automatic evaluation of Kikuchi diffraction patterns gives the complete information about the 3- dimensional orientation of the single particles and sub-grains, and can distinguish between the different types of secondary phases with the information of their lattice point groups. The goal of the EBSD measurements is the simultaneous determination of sub-grain and particle sizes, orientations and dislocation densities. The advantage of EBSD is the opportunity to analyse the measurements automatically- the locations of sub-grain boundaries are much easier to find in an orientation map than in a TEM image. There a sub-grain boundary is defined as a misorientation between two neighbouring regions that exceeds a critical misorientation angle (15° for grain boundaries, >5° for sub-grain boundaries).

An important parameter for the nucleation and growth of precipitates and for the calculation of grain boundary energies is the misorientation on subgrain boundaries and particle interfaces. A decrease of the systems energy can be a result from a decrease of the total area of boundary surfaces or a shift in the orientations of sub-grains and particles and thus in the misorientations of the boundaries. The energy of sub-grain boundaries can be calculated for symmetrical tilt boundaries and small angles as a function of the tilt angle  $\theta$  by the Read- Shockley equation:  $\gamma_{gb} = E_0 \cdot \theta \cdot (A_0 - \ln \theta)$  [1], for bigger (>15°) misorientation angles several minima in the surface energy due to twin boundaries can be found. To describe the conditions of particle nucleation and growth thoroughly, measurements of the location of precipitates relative to sub-grain boundaries and dislocation structures are necessary, as well as the misorientation of the sub-grains and precipitates. several minima in the surface energy due to twin boundaries can be found. To describe the conditions of particle nucleation and growth thoroughly, measurements of the location of precipitates relative to sub-grain boundaries and dislocation structures are necessary, as well as the misorientation of the sub-grains and precipitates.

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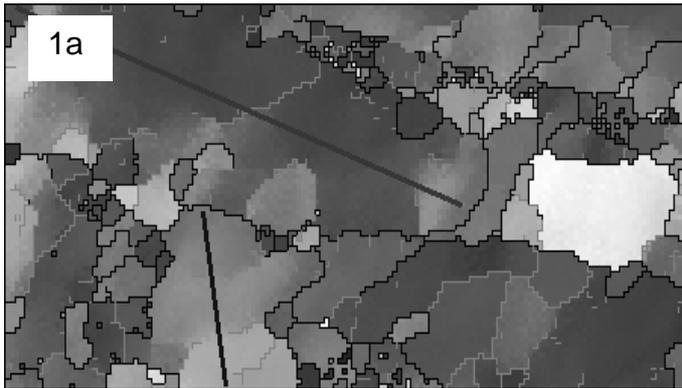


Fig. 1: High resolution orientation map of a rot rolled Iron bcc- phase sample with inverse pole figure encoding the colour map [2]

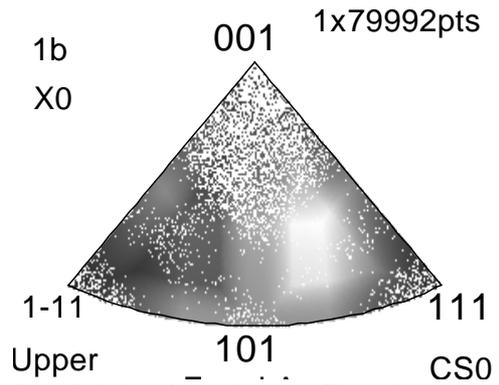


Fig. 2: Misorientation profiles along the red line in fig.1. In graph 2a, the misorientations are relative to the point before; in graph 2b they are relative to the first point

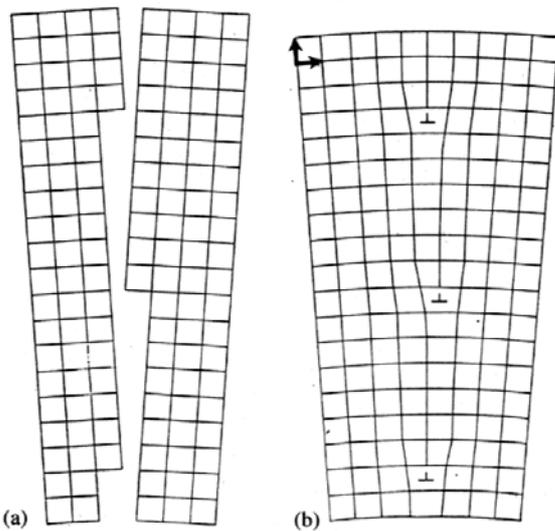
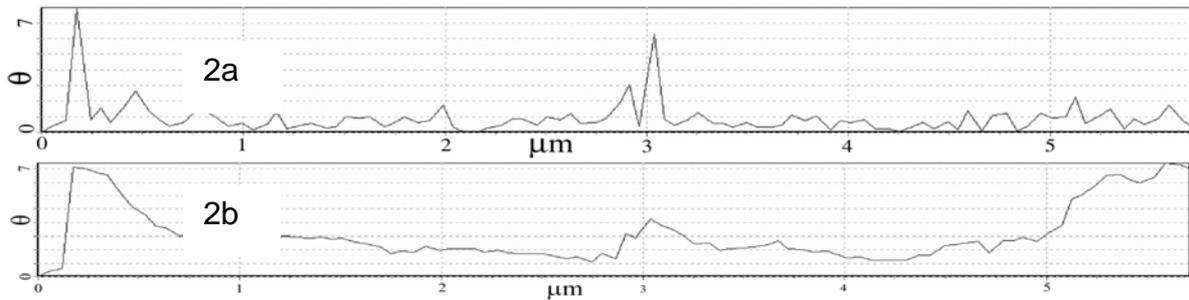


Fig. 3: Schematical plot of a symmetrical tilt boundary

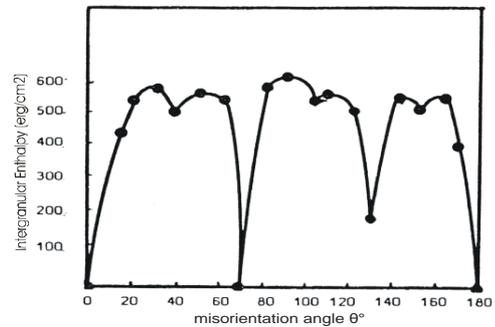
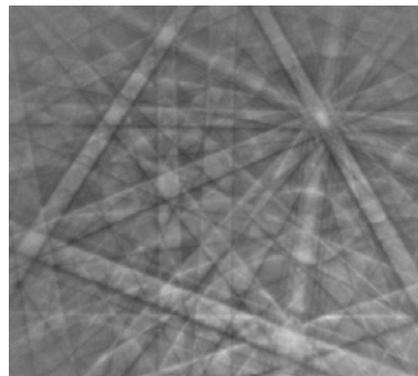


Fig. 4: Calculated boundary energy of a symmetrical tilt boundary of an aluminium fcc grain boundary; critical angles for twin boundaries are visible at energy minima.

Fig. 5: Typical Kikuchi – pattern of an iron bcc phase



## Synthesis of Multicomponent Nano-Particles with an Aerosol Reactor – Reference Materials for SEM / EDXS Analyses

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In the attempt to analyse the morphology and chemistry of smaller and smaller features or particles from various samples (e.g. environmental samples) by SEM / EDXS, it is an absolutely essential prerequisite to have adequate standard reference materials. These particle standards should resemble the samples in size, shape and composition. Unfortunately, commercially available particle standards cover mainly the region above 1  $\mu\text{m}$  with sometimes-irregular shapes and often do not contain elements in the desired composition and concentration. In addition to the described feasible ways<sup>1</sup> to produce submicron- or nanometer-scaled homogeneous particles, this work uses the advantages of the aerosol production method<sup>2</sup> to create the desired materials.

Submicron ternary  $\text{SiO}_2\text{-TiO}_2\text{-Fe}_2\text{O}_3$  particles were produced by thermal decomposition of precursor droplets in a heated tube reactor (VTF 40-12, Entech). Precursor droplets were dispersed in nitrogen by a constant output atomizer (TSI 3076, TSI Inc.) and subsequently diluted with air. The aerosol was further carried to the heated tube furnace, where the particles were formed at defined temperatures. The ethanolic precursor solution consisted of titanium-tetra-isopropoxide (TTIP), tetra-ethyl-orthosilicate (TEOS) and iron nitrate with elemental ratios of  $\text{Si/Ti} = 3$  and  $\text{Si/Fe} = 6$  in wt-%. The particle size distribution was determined with a differential mobility analyser (DMA, TSI 3071) and with a condensation nucleus counter (CNC, TSI 3022). Gas-phase TEM samples were collected with electrostatic precipitator (ESP, InTox Products) on holey carbon coated copper grids. SEM samples were collected on Nuclepore filters within preset collecting times, to obtain optimum particle distribution rates. The sample morphology, composition and crystallinity were studied with transmission electron microscopy (TEM, Philips CM20 and Philips Tecnai F20). Additional ICP measurements were performed to confirm the elemental ratios in the precursor solution and the produced particles.

TEM investigations of particles produced at 1200°C revealed crystalline inhomogeneities within the particles, which was also found by Ehrmann<sup>3</sup> for the two-component system  $\text{SiO}_2\text{-TiO}_2$  produced in a premixed flame. This inner structure was determined by EFTEM elemental maps (Fig.1) and selected area diffraction (Fig.2) to consist of hematite and rutile crystallites within a  $\text{SiO}_2$  matrix. The particles showed a mean diameter of around 90 nm, which could be slightly increased by decreasing the temperature of the tube reactor. By decreasing the temperature (800°C) also the size of the crystallites could be reduced to such small dimensions that the used characterisation methods (EFTEM and selected area diffraction) could only determine a homogeneous distribution of the predicted elements.

The produced particles were used as reference materials for the evaluation of conventional SEM / EDXS quantification routines (e.g. ZAF, PROZA) and special designed particle correction procedures<sup>4</sup>.

Due to the advantages of the proposed aerosol production method (perfect spherical shape, variety of elemental combinations, homogeneity) many other possible applications may be considered.

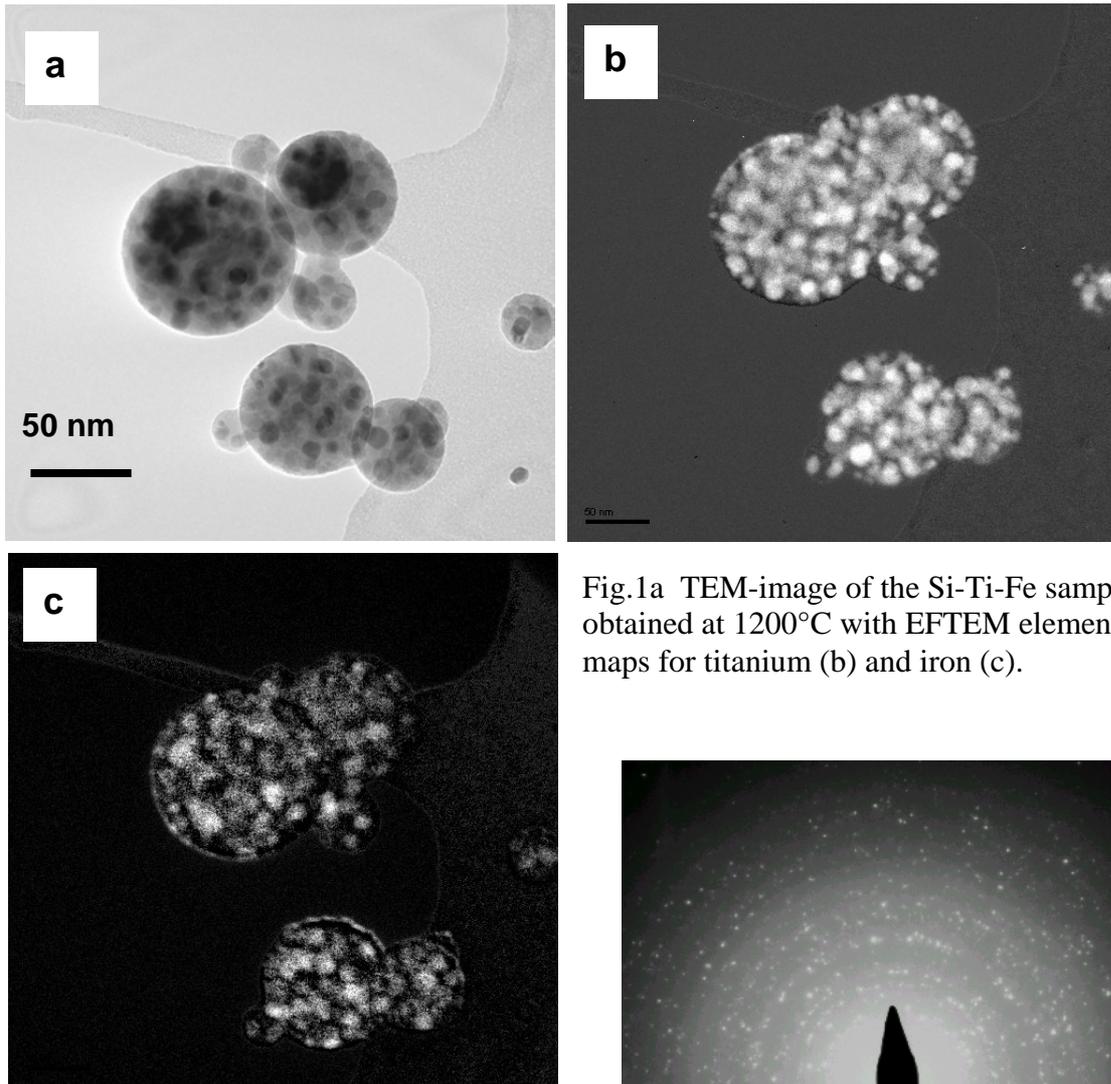


Fig.1a TEM-image of the Si-Ti-Fe sample obtained at 1200°C with EFTEM elemental maps for titanium (b) and iron (c).

Fig.2 Selected area electron diffraction of the 1200°C Si-Ti-Fe sample.



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## Micro Raman Spectroscopy: An Appropriate Method for the Characterization of Orientation and Crystallinity of Polypropylene

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With an annual production of about 22 million tons polypropylene (PP) belongs to the most important synthetic materials. The wide range of applications and the great diversity of PP products concerning optical and mechanical properties demand a deep understanding of the materials properties. Fillers and additives are used for fine-tuning but the morphology is the main factor for controlling the final properties. In a semi-crystalline polymer it is controlled by the degree of chain orientation and crystallization. Furthermore the need of a fast and non-destructive characterization method for online analysis is growing and Raman spectroscopy seems to be an appropriate tool.

Raman spectroscopy is an excellent method for conformational analysis. Thus it is possible to determine the orientation of polymer chains within a sample. Even tacticity and amorphous contents can be identified using Raman spectroscopy. In our work we concentrated on polypropylene fibers. It was our goal to identify all Raman bands in the region between 800 and 1550 $\Delta\text{cm}^{-1}$ , which are influenced by the orientation of the fiber with respect to the polarization of the incoming laser light. The other regions, mainly the one below 3000 $\Delta\text{cm}^{-1}$ , were not considered because of strong peak overlapping and a more complicated evaluation of peak areas. To obtain the desired information a number of measurements under different sample orientation were performed. In this way we could obtain a rotational profile as shown in fig. 1, where only two wavenumber regions were selected. Spectra of a polypropylene fiber over the whole range of interest are shown in fig. 2, where orientation was changed by 90 degrees.

The other very important characteristic quantity in describing the sample morphology is the degree of crystallinity. Experiments in a hot/cold cell were performed and the peak intensities were observed over a wide temperature range. Disappearance of some peaks and a general broadening could be observed upon heating the sample. From the molten sample we could obtain data of non-oriented polypropylene. Under the assumption that orientation of chains can be neglected, when a melt is rapidly cooled from the liquid state to room temperature but under different shear conditions, we also registered spectra of semi-crystalline polypropylene with different degree of crystallinity but no orientation at all. This was very important in order to combine Raman information of orientation and crystallinity, which is necessary for investigations on injection molded samples, films or fibers as they are used in industry.

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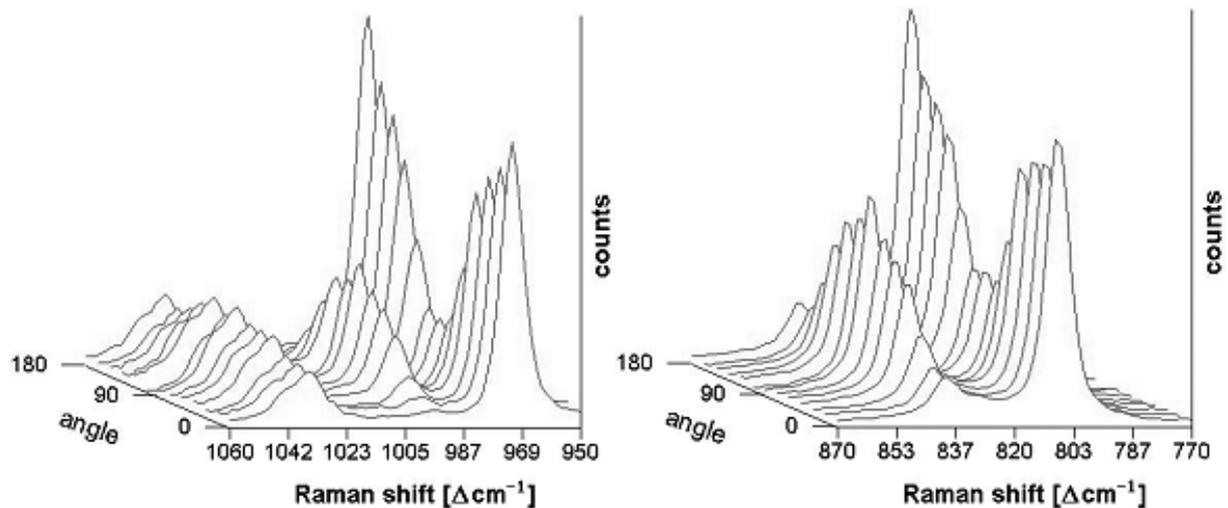


FIG. 1: Dependence of Raman band intensity from the angle between fiber and incoming laser polarization. The difference in angle between each spectrum is 15°.

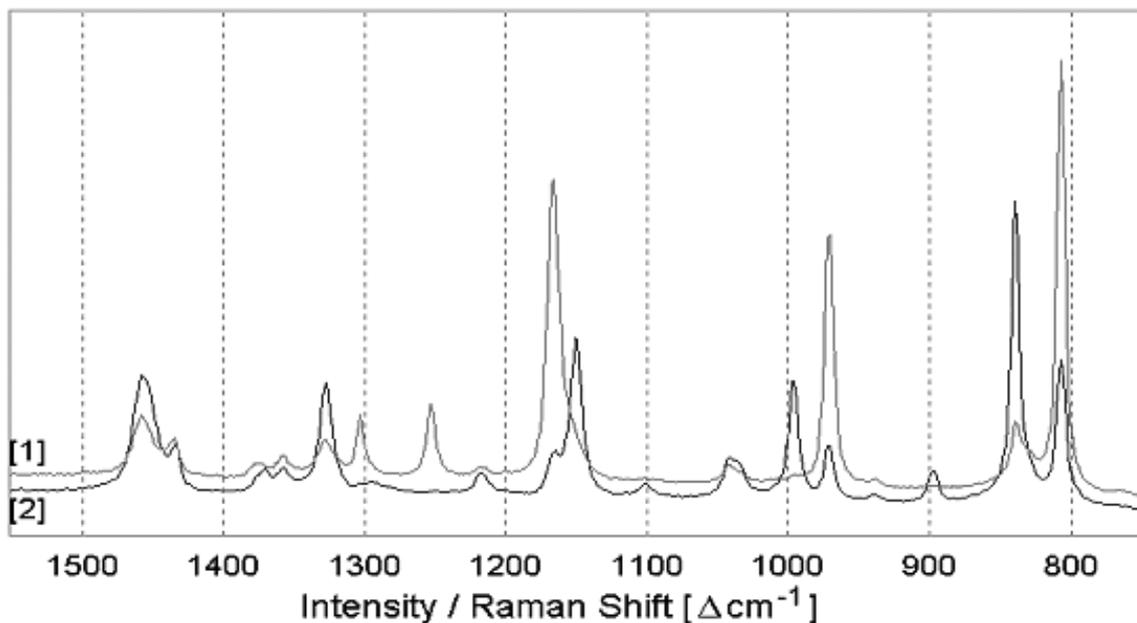


FIG. 2: Changes of band intensities in the Raman spectrum of polypropylene due to sample orientation. [1] Fiber is parallel and [2] perpendicular to incoming laser polarization.

## Degradation of Poly(vinyl chloride) with Different Additives Studied by Micro Raman Spectroscopy

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Poly(vinyl chloride) is one of the most important synthetic materials. Its properties make it ideal for long-lifetime and high stability applications. These very desirable properties can be achieved by adding various chemical substances amongst them chemical stabilizers. They can greatly influence heat, oxygen or UV radiation resistance. Although there are many PVC products available on the market and the technology is known for several decades now, the working principle of most stabilizers is still unknown. Investigations on this field and a deeper understanding of the chemical backgrounds can help optimizing the stabilizer mixture, hence reduce costs and contribute to a more ecological operating chemical industry.

One method of PVC degradation is based on the formation of conjugated double bond sequences, which cause discoloration and on a higher level a complete destruction of the material, when reactions with the labile double bonds take place. Raman spectroscopy is an analytical method, which allows the detection of such conjugated double bond sequences along the polymer backbone at a level of around  $10^{-5}$  %, which translates into the very first stage of thermal degradation. The reason for this extremely high sensitivity is explained by the so-called resonance Raman effect. In our work we used this enhancement of the band intensity for the C=C and C-C stretching vibrations to follow the degradation process as a function of temperature. PVC granules in its native form as well as ones mixed with different additives were put into a hot/cold stage and heated up to temperatures of 160°C. Another effect used in this was the amount of fluorescence, as an indicator for sample destruction. During these investigations we could draw some conclusions on the working principles of some additives and determine their influence on the stabilization process.

As additives to the native PVC we chose calcium stearate and zinc stearate, which are commonly used stabilizers in PVC industry. Figure 1 shows the degradation of native PVC with increasing temperature. The first spectrum in the front of the image has been acquired at 75°C and the last one in the back at 160°C. Step size for spectra acquisition was 5°C. It is clearly visible that the number of conjugated sequences increases at higher temperatures. In the back also a slight fluorescence background is visible, which can be understood as polymer destruction. All diagrams presented here provide Raman information [ $\text{cm}^{-1}$ ] on the x-axis, signal counts on the y-axis, and the sample temperature at which the spectra were registered on the z-axis. Figure 2 provides the degradation diagram of the same native PVC material with 1 phr zinc stearate. The zinc soap reacts with liberated HCl under formation of inert  $\text{CaCl}_2$  and fatty acid. Both products don't support further degradation and the materials destruction initiated by HCl is slowed down. The effectiveness of the stabilization system can be seen in the signal ratio comparing figure 1 and 2: 200,000 versus 30,000 means a quite good improvement in terms of PVC stabilization, as signal counts are proportional to the present number of conjugated sequences. Figure 3 shows the degradation process of native PVC with 1 phr zinc stearate. In this case fatty acids will be removed by chlorine atoms of liberated HCl and the rate of degradation is lowered by the same phenomenon as before. In contrast to  $\text{CaCl}_2$ , zinc chloride is a strong Lewis acid, which accelerates the abstraction of labile chlorine atoms under formation of zinc chloride complexes. When the reservoir of fatty

acids is exhausted no HCl can be fixed anymore and additionally  $ZnCl_2$  boosts the degradation process. This behavior can be seen in figure 3 by the tremendous increase of background fluorescence. It could be proved that Raman spectroscopy enables observation of the first stage of thermal degradation, which is not accessible with any other technique.

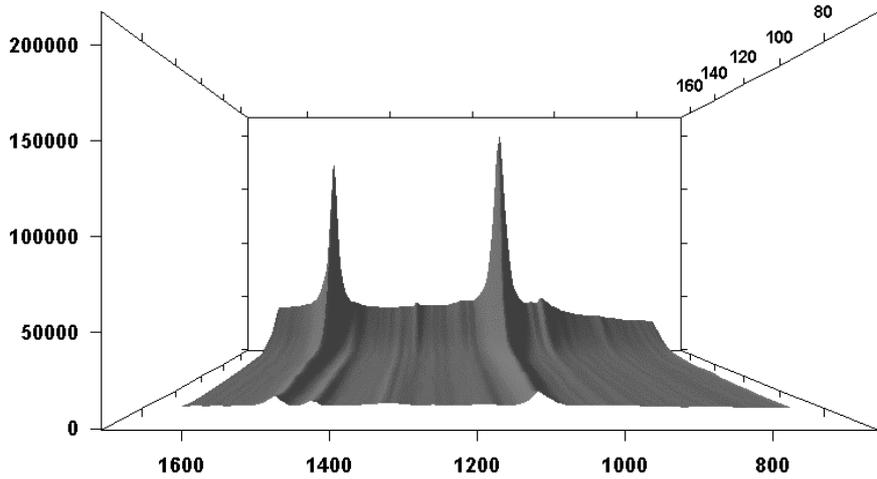


Figure 1: Degradation process of pure PVC with time.

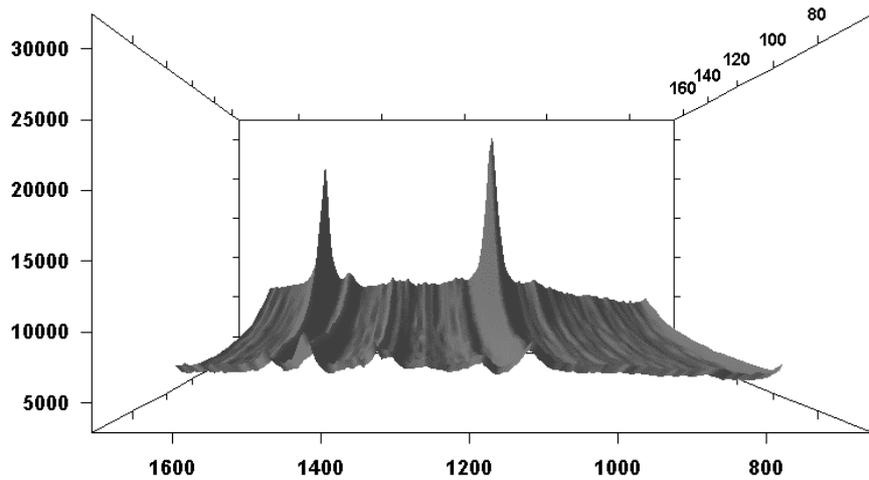


Figure 2: Degradation process of pure PVC with 1 phr calcium stearate.

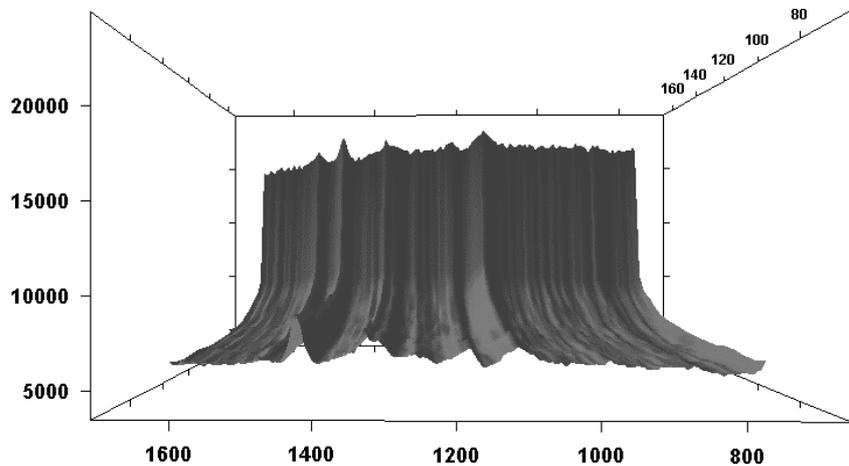


Figure 3: Degradation process of pure PVC with 1 phr zinc stearate.

## Methanol Crossover Suppression in Direct Methanol Fuel Cells by Sub-Micron Palladium Layers

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Methanol crossover occurring in direct methanol fuel cells [1] is still one of the major problems in the current fuel cell technology. Strategies to reduce or even eliminate methanol crossover focus on improved solid polymer electrolytes [2], cathode catalysts [3] and – probably the most promising way - the application of methanol impermeable but hydrogen permeable layers of metallic palladium [4].

For the fuel cell experiments a testing cell was designed consisting of modular components, which can be easily exchanged. The anode chamber was connected to an electrolyte storage tank and the electrolyte was permanently circulated to provide a constant concentration of methanol in the anode chamber. The cathode chamber was equipped with a sampling interface for methanol analysis. Under operating conditions it was filled with methanol free liquid electrolyte. The methanol crossover was monitored by measurement of the methanol concentration in the cathode chamber using a specially developed GC-SPME method [5].

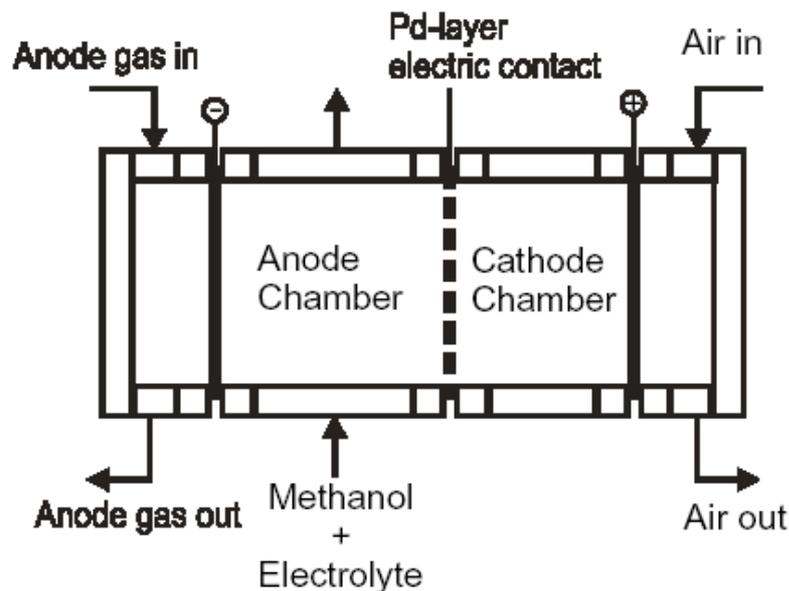


Fig. 1: Sketch of the test cell, the electrodes are quickly replaceable as well as the unit holding the membrane.

Nafion 117 membranes were coated with thin layers of palladium by means of electroless plating. Activating solution Neoganth® and palladium electroless plating solution Pallatect PC® were provided by Atotech. According to ESEM micrographs coherent and pinholefree layers having a thickness of about 0.3µm were obtained (Fig.2). The images of the palladium could only be recorded in ESEM mode (4.6Torr, 2°C, “wet” conditions), where the drying of the wetted membrane and thus shrinking is prevented.

Galvanostatic measurements in the test cell at low temperatures showed a higher cell voltage, when plated Nafion® was used as a separator, while a decreased methanol concentration was measured in the cathode chamber by GC-SPME analysis.

Experimental results indicate that Nafion® membranes coated with palladium by electroless metallisation suppress methanol crossover and thus enhance DMFC cell performance.

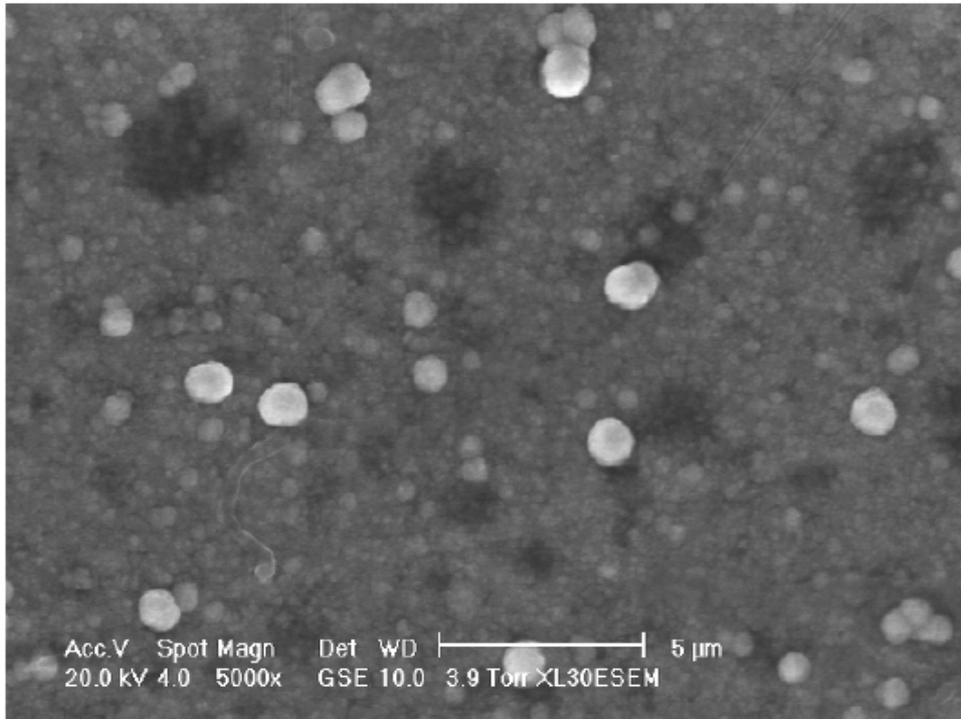


Fig. 2: ESEM picture showing a piece of palladium coated Nafion membrane wetted before submitting to analysis.

Financial support by the Austrian Science Fund (FWF) in the "Electroactive Materials" special research programme is gratefully acknowledged.

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## EFTEM at High Magnification: Principles and Practical Applications

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Energy-filtering TEM (EFTEM) has proven to be an efficient technique for determining elemental distributions on a nanometer length scale. Especially, post-column energy-filters in combination with high resolution TEMs can provide the capability to detect and separate small features down to subnanometer regions [e.g. 1, 2, 3; fig. 1]. Far more than in high-resolution TEM, the attainable spatial resolution is influenced by the experimental setup: The energy and the shape of the ionization edge, as well as experimental parameters like the collection angle, influence the obtainable resolution together with instrumental parameters (aberration coefficients of the TEM objective lens) [4, 5]. Additionally to these theoretical limitations, however, there are practical aspects, that also limit the resolution in EFTEM: maximum electron dose, exposure time, specimen drift and instrumental instabilities. When considering, that at high magnifications only a small number of atoms (typically 10 – 1000) contribute to the signal in a pixel of the final image, it is obvious that accurate instrumental alignments and a careful experimental setup are paramount for good quality results. It should also be noted, that a certain amount of elastic contrast is always transferred to energy-filtered images [6], which can lead to artifacts in elemental distribution images.

In this study we present results obtainable with high resolution EFTEM. Fig. 1 shows an elemental map (three window technique) of a Mn/PdMn multilayer using the Mn-L<sub>23</sub> ionization edge acquired on a 200 kV FEG-TEM with a post-column energy filter. The Mn layer thicknesses are between 2.6 and 0.47 nm, the thickness of the PdMn spacer layer is constant (3.7 nm). The integrated profile across the image shows peaks for every single layer. As the layers get thinner, the widths of the peaks remain constant for layer thicknesses below about 1.5 nm. For thinner layers the area under the peak decreases, until it may reach a level, where it cannot be longer distinguished from noise (estimated to be around 0.16 nm for the acquisition parameters used in fig. 1).

For many applications it is important to characterize thin oxide layers, e.g. in semiconductor devices, which nowadays reach thicknesses of just a few monolayers. The thickness of such layers in semiconductor devices plays an essential role in the functionality of the device. Using the contrast difference between the Si substrate and the thin silicon oxide layer at certain energy losses, the oxide layer can be imaged at nm resolution (fig. 2). At the low energy-losses used (30 – 90 eV) the signal to noise ratio is very high, which allows short acquisition times. However, at these low energy-losses delocalization is decreasing the resolution to values of a couple of nm. Our work will be presented how to account for this broadening, and to remove it digitally in order to improve the resolution.

The dimensions in many materials science devices become smaller and smaller, that's why the reliability of compositional profiles is an important issue. EFTEM provides a quick analytical tool for such investigations, but in some cases its applicability may be limited due

to the limited spatial resolution. In this paper we highlight these limitations as well as the prospects of the technique.

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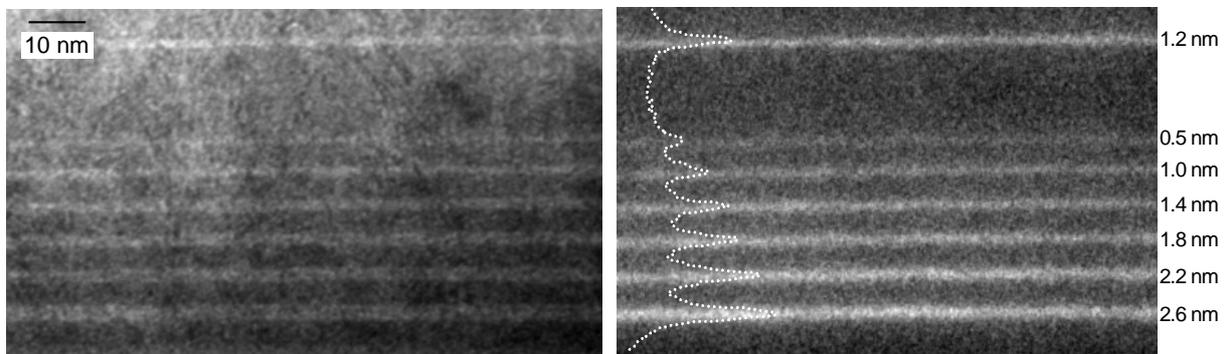


Fig. 1: Bright field image (left) and Mn-L<sub>23</sub> elemental map (right) of a Mn/PdMn multilayer. The thinnest Mn layer is 0.5 nm thick. The elemental map was calculated from energy-filtered images at 607, 627 and 650 eV with a 20 eV slit and an exposure time of 20 s.

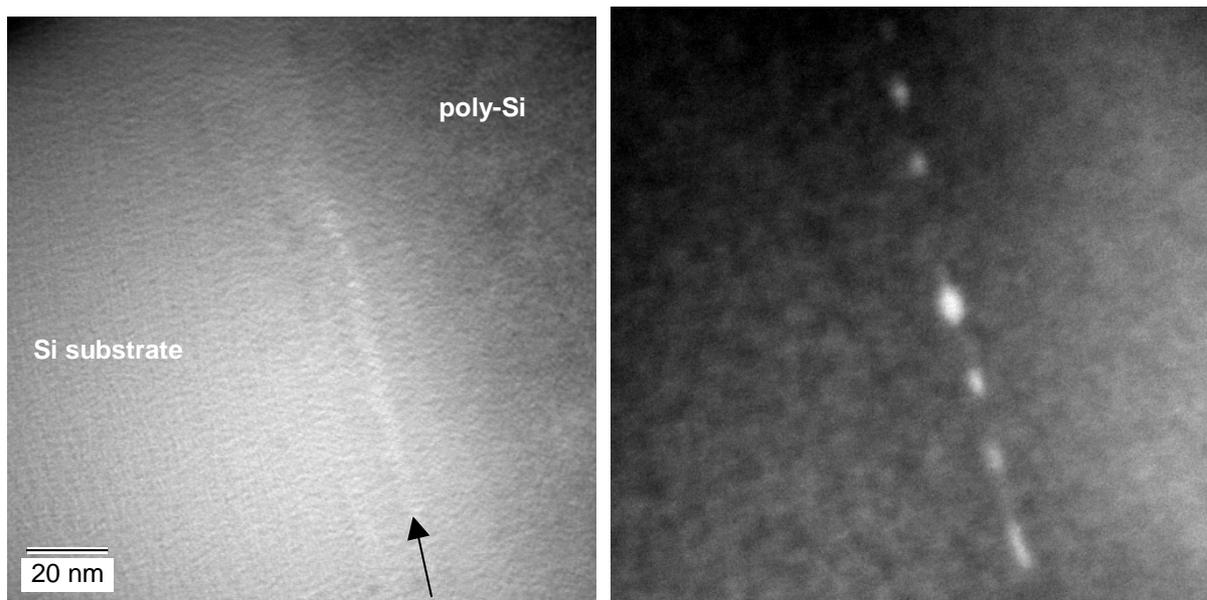


Fig. 2: Bright field image (left) and energy-filtered image at 30 eV (10 eV slit, right) of a thin oxide layer (arrow) on a Si substrate underneath an originally amorphous silicon layer, which was subsequently recrystallized by annealing at 1000 °C. Using EFTEM the nominally 1 nm thin oxide layer could be detected and an insular growth confirmed.

## Low-Loss EFTEM for Imaging of Thin SiO<sub>2</sub> Layers in Silicon Based Devices: Image Contrast as a Function of Sample Thickness

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Energy filtering transmission electron microscopy (EFTEM) is now a known method for recording images carrying elemental and chemical phase contrast. EFTEM images are usually recorded at energy-losses in front of and after ionization energies of the elements under investigation and are then combined into elemental distribution maps [1,2,3,4,5]. However, these elemental maps show weak signal intensities and thus a small signal-to-noise ratio (SNR) due to the small inner-shell cross sections. This is a severe limitation whenever small features should be imaged and high magnification is needed [6].

Other groups showed that low-loss images also carry material specific information and can therefore be used for chemical phase mapping [7,8,9,10]. Signal intensity in such low-loss images is generally much higher and in certain cases good material contrast can be achieved though diffraction contrasts in crystalline materials limit the practical applicability. However, the material contrast depends on a variety of parameters which need to be investigated in detail for different material combinations.

In this work we examined the combination of the industrially important materials silicon and silicon dioxide as they appear in many semiconductor devices e.g. in metal oxide field effect transistors (MOSFETs). In a MOSFET the thin SiO<sub>2</sub> layer acts as an insulator between the semiconductor channel (Si) and the gate. Such isolating layers are currently approaching thicknesses of few nanometers and reliable quality characterizations will play an important role in the future development of the devices. Since elemental mapping using the core-losses is limited due to the low SNR in the maps, we systematically investigated the alternative imaging possibilities in the low-loss region below the Si-L<sub>2,3</sub> edge where images show material contrast between the two materials. We developed two methods to calculate contrast as a function of the important parameters sample thickness and energy-loss. The resulting contrast map was used to determine the ideal imaging conditions to obtain optimum SNR. Both methods, though developed for this specific material combination, can be applied to a variety of material combinations in order to systematically investigate EFTEM imaging in the low-loss region.

For the Si/SiO<sub>2</sub> combination the ideal recording parameters in the low-loss region were determined. Either a 5 eV slit at an energy-loss of 16 eV or an 20 eV slit at an energy-loss of 80 eV yield optimal results concerning material contrast. Sufficient resolution of better than 2 nm could be achieved in both regions. Pronounced delocalization effects could not be observed.

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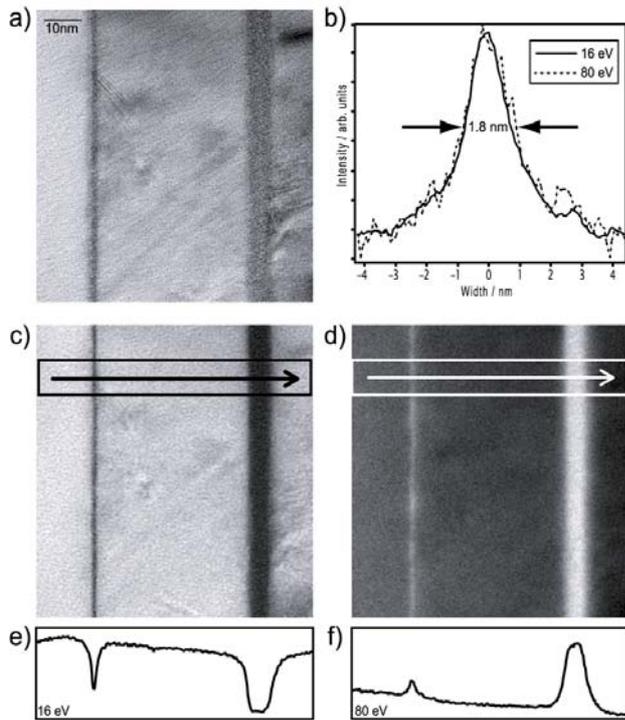


Fig.1  
 a. TEM bright field image of a layer stack (Si-wafer/SiO<sub>2</sub>/poly-Si/SiO<sub>2</sub>/poly-Si)  
 b. comparison of layer thickness of the thinner SiO<sub>2</sub> layer measured in both EFTEM images  
 c. EFTEM image at 16 eV energy-loss  
 d. EFTEM image at 80 eV energy-loss  
 e. Line profile taken from the indicated area in c)  
 f. Line profile taken from the indicated area in d)

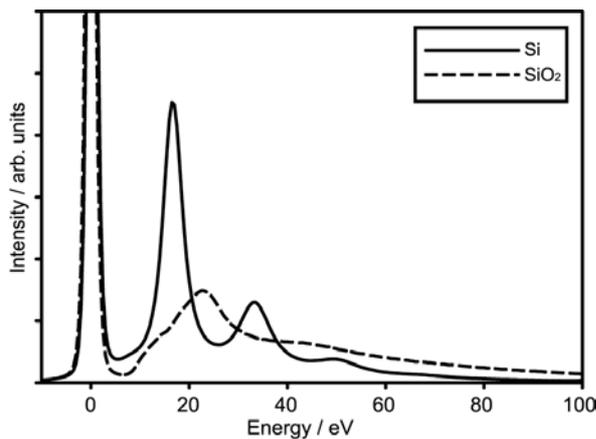


Fig.2  
 EELS spectra of Si and SiO<sub>2</sub>

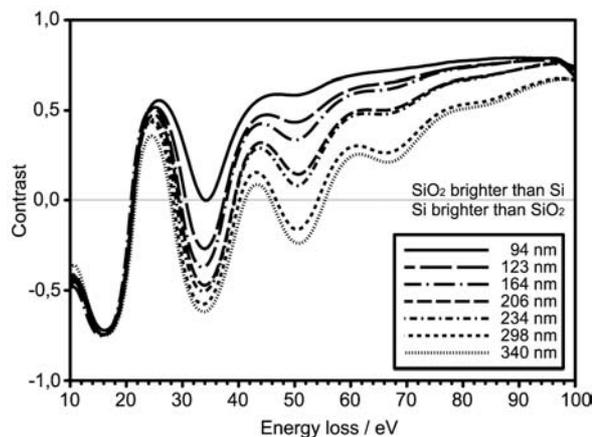


Fig. 3  
 Material contrast between Si and SiO<sub>2</sub> as a function of specimen thickness and energy-loss

Financial support by the Austrian Science Fund (FWF) in the "Electroactive Materials" special research programme is gratefully acknowledged. We thank Austriamicrosystems AG, Schloss Premstätten, A-8141 Unterpremstätten, Austria for preparing the semiconductor sample.

## High Energy Resolution EELS using a Monochromized 200 kV TEM: Comparative Investigation of the Ti $L_{2,3}$ edge of Rutile ( $\text{TiO}_2$ )

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Although it is well known that EELS near edge fine structures are a powerful tool for studying chemical bonding at the nanometer level, important applications were prohibited due to the limitation of the initial energy width of the source which is typically 0.6 eV for Schottky emitters. If the energy resolution can be improved towards the 0.1 eV regime, near edge fine structure details can be revealed not previously observable by EELS in common instruments.

To address this, FEI has constructed a monochromized 200 kV (S)TEM which aims at 0.1 eV energy resolution in EELS. The improved energy resolution is due to several factors: (a) The energy spread of a Schottky field emitter (typically 0.6 eV) is reduced by a Wien filter monochromator positioned directly after the field emission gun<sup>1</sup>. (b) The development of a high resolution energy filter for the monochromized TEM by Gatan featuring new high stability electronics and four additional multipoles<sup>2</sup>. (c) The 200 kV high tension tank was improved by adding mechanical as well as electrical damping elements<sup>3</sup>.

The main objective of this study is to check the performance of this monochromized (S)TEM with a well characterized sample and to compare these results with previous experiments. For this purpose, rutile ( $\text{TiO}_2$ ) was chosen having a tetragonal structure, the unit cell containing two titanium and four oxygen atoms. The coordinating oxygen octahedron around the titanium atom is slightly distorted with two different bond lengths. The local point-group symmetry around the titanium atom is  $D_{2h}$ <sup>4</sup>. The rutile crystals were crushed in an agate mortar and dispersed on holey carbon grids.

The first measurements were carried out on a 200 kV Philips CM20 TEM with a  $\text{LaB}_6$ -cathode (undersaturated), equipped with a Gatan Imaging Filter (GIF), with a measured energy resolution of 0.65 eV at the zero loss peak. Additional measurements were performed on a TECNAI F20 field emission microscope with nominally 0.7 eV resolution and the monochromized TECNAI F20 at 200kV. These data were compared with an EELS-spectrum recorded at the Fritz-Haber-Institute in Berlin, with a dedicated STEM fitted with a cold field emission gun, a sector field spectrometer and a parallel recording system (energy resolution  $\sim 0.3$  eV)<sup>4</sup>.

The experimental spectra are given in fig.1. Due to spin-orbit splitting the  $L_3$  and the  $L_2$  edges are widely separated. The white lines themselves split by the crystal field effect into  $t_{2g}$  and  $e_g$  orbitals. The separation of the  $e_g$  orbitals reflects a decrease of symmetry due to the distortion of the  $[\text{TiO}_6]$ -octahedra in rutile. The two small pre-peaks correspond to a spin-forbidden transition to a triplet state.

The main spectral features of the Ti  $L_{2,3}$  edge can be revealed even with a  $\text{LaB}_6$  TEM; for the first time the  $e_g$  splitting was measured with a  $\text{LaB}_6$  microscope. However, most fine structure details are only accessible with the FEG instruments, where the monochromized TEM exhibits a significantly better separation of the spectral features. The first line in

spectrum (c) has a width of 0.4 eV which is very close to the natural line width due to core-hole life time broadening (approximately 0.2 eV in the  $t_{2g}$  peak at the Ti  $L_3$  edge). It is obvious that energy-resolution in the range 0.2 to 0.3 eV is sufficient to reveal the most important fine structure details. In this case further improving of the resolution would not increase the information, since core hole life time broadening smears out finer spectral features. Consequently, the monochromized 200 kV (S)TEM will greatly improve our ability to use ELNES as a source of chemical bonding information at high spatial resolution.

Financial support by the Austrian Science Fund (FWF) in the "Electroactive Materials" special research programme is gratefully acknowledged.

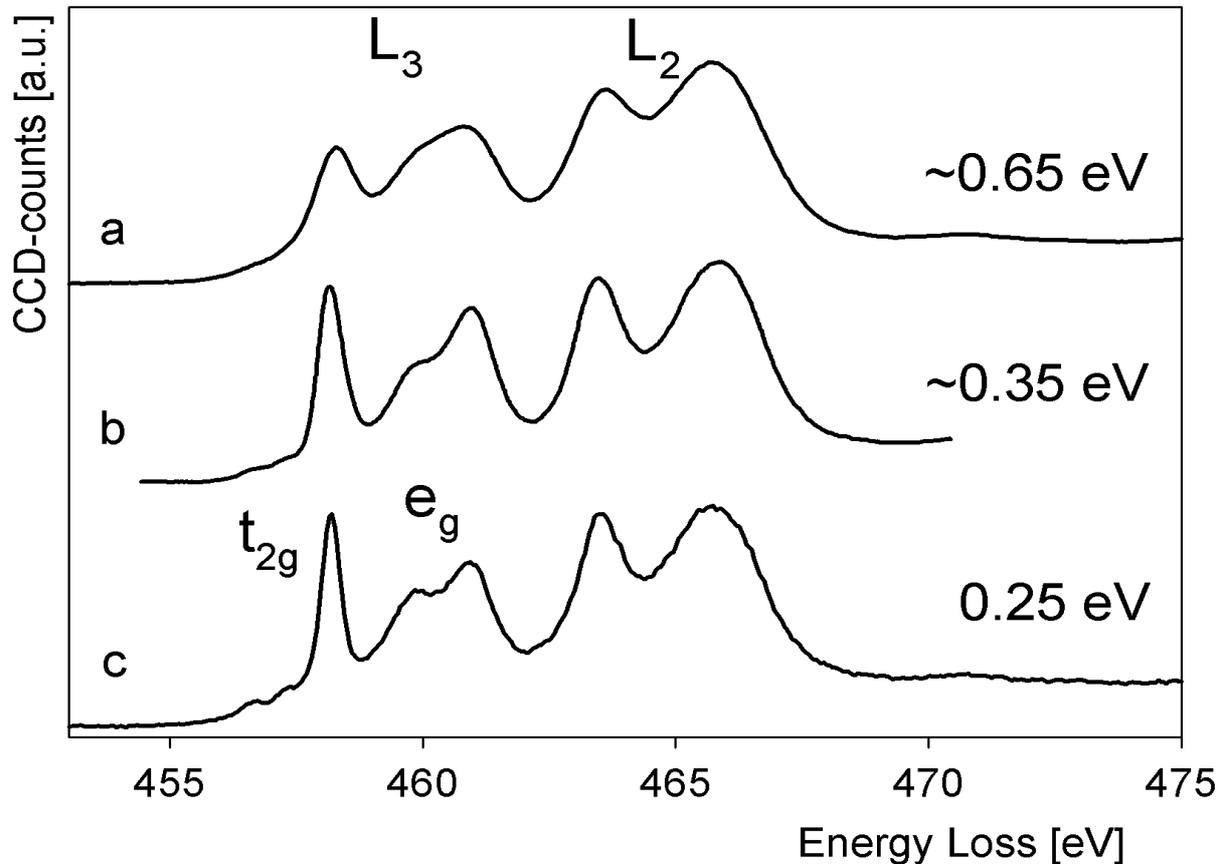


Fig.1 The experimental spectra of the Ti  $L_{2,3}$  edge in rutile a. CM20 (200 kV, LaB<sub>6</sub>); b. STEM-PEELS-system (60 kV, FEG); c. Tecnai F20 (200 kV, Schottky emitter with HR-GIF and monochromator).

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## Comparative ELNES Measurements on Selected Transition Metal Oxides on a New High Energy-Resolution Spectrometer / Monochromator TEM

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Although it is well known that EELS near edge fine structures (ELNES) are a powerful tool for studying chemical bonding at the nanometer level, important applications were prohibited due to the limitation of the initial energy width of the source, which is typically 0.6 eV for Schottky emitters. If the energy resolution can be improved towards the 0.1 eV regime, near edge fine structure details can be revealed not previously observable by EELS in common instruments.

To address this, FEI / Gatan has constructed a monochromized 200 kV (S)TEM which aims at the 0.1 eV energy resolution level for EELS. The improved energy resolution is due to several factors: (a) The energy spread of a Schottky field emitter is reduced by a Wien filter monochromator positioned directly after the field emission gun. (b) The 200 kV high tension tank was improved by adding mechanical as well as electrical damping elements [1], and (c) a high resolution energy filter delivers more stable electronics as well as improved electron optics [2]. The electron optics of the spectrometer as installed at the FELMI now comprises additional multipole lenses in front of the magnetic prism, which eliminate 3<sup>rd</sup> and some of the 4<sup>th</sup> order spectral aberrations. The electron optical performance of the spectrometer can be represented by its isochromatic surface as displayed in fig. 1. It shows the relationship between the spectrometer collection angle (implicitly expressed by the size of the indicated apertures) and the focussing error of the spectrometer. The filter can now accept maximum scattering angles, which are about 70% larger compared to conventional post-column filters without compromising energy resolution. Larger spectrometer entrance apertures in combination with further reduced camera lengths result in a system with considerably improved collection efficiency for EELS measurements, giving spectra of higher quality especially on dose sensitive samples.

The main objective of this study is to check the performance of the new spectrometer on a monochromized and unmonochromized 200kV FEG (S)TEM with a well characterized sample and to compare these results with previous experiments. For this purpose, vanadium oxide (V<sub>2</sub>O<sub>5</sub>) was chosen for its challenging fine-structure at the V 2p(3/2) and V 2p(1/2) peaks and for its known sensitivity for reduction under the electron beam [3,4]. V<sub>2</sub>O<sub>5</sub> has an orthorhombic structure, with vanadium being surrounded by six oxygen atoms, forming a distorted octahedron. The L<sub>3</sub> and L<sub>2</sub> peaks are further split into doublet features as a consequence of an octahedral ligand-field splitting, which divide the d-state into t<sub>2g</sub> and e<sub>g</sub> orbitals. Although the L<sub>3</sub> and L<sub>2</sub>-edge of TiO<sub>2</sub> (the neighbouring d<sup>0</sup> oxide) show well-resolved t<sub>2g</sub>-e<sub>g</sub> features, the energy separation for V<sub>2</sub>O<sub>5</sub> does not have the same value and in fact is only in the order of the energy resolution of a typical FEG TEM at around 0.8 eV [5]. Experimental spectra of V<sub>2</sub>O<sub>5</sub> taken on different instruments are displayed in fig. 2. While the basic shape of the V L<sub>2,3</sub> edge comes out clearly on all instruments, most fine structure details

are only observable with field-emission instruments, where the monochromized TEM exhibits a significantly better separation of the spectral features. The paper intends to demonstrate the usefulness of the new spectrometer/monochromator combination for ELNES measurements applied to technologically relevant transition metal oxides.

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Fig. 1: Extrapolated experimental isochromatic surface of the high resolution EELS spectrometer at 200 kV. Apertures are drawn as circles. Measurements indicate that for a practical total energy resolution of 0.3 eV on a monochromated microscope, a 3 mm aperture can still be used.

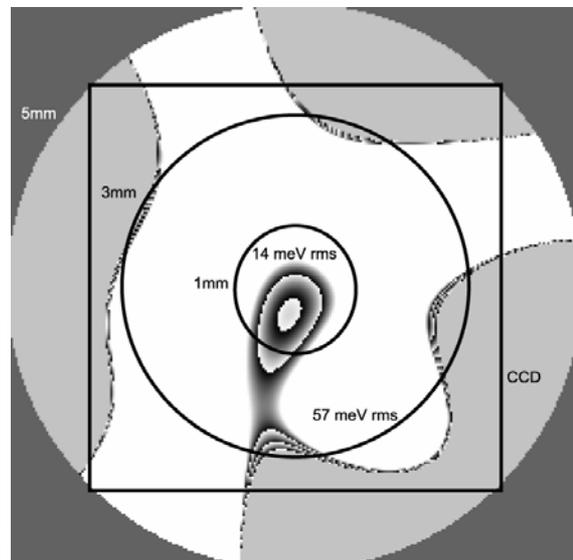
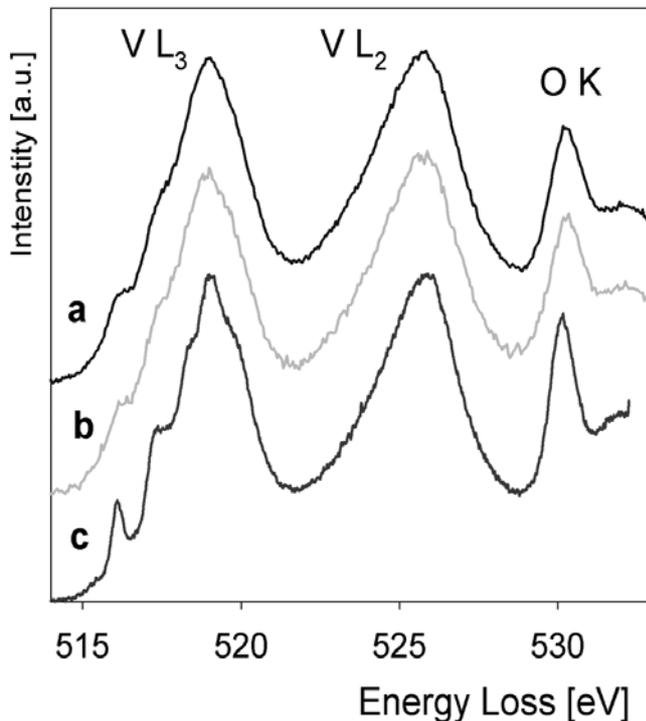


Fig. 2: Experimental EELS spectra from  $V_2O_5$ ; a. recorded on a FEI CM20/ LaB<sub>6</sub> / GIF200 (top), b. Tecnai F20 FEG with a high-resolution spectrometer and c. Tecnai F20 / monochromator. The  $t_{2g}-e_g$  ligand field splitting of 0.8 eV being clearly revealed only on the monochromated microscope.

Acknowledgements:

M. Barfels and P. Burgner from Gatan provided essential technical help on the HR-GIF. M. Hävecker and A. Knop-Gericke from Berlin are gratefully acknowledged for the specimen preparation. We also thank H. Zandbergen for giving access to the monochromator microscope and C. Mitterbauer from the FELMI.

## ELNES as a Fingerprint for Identifying Chromium Nitrides

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The near edge fine structure in electron energy-loss spectrometry (EELS) contains information about the local bonding and environment of atoms in solids. The ELNES (Energy Loss Near Edge Structure) arises because the final states of the excitation process are unoccupied states above the Fermi level which may be appreciably modified by chemical bonding<sup>1</sup>. One approach to understanding ELNES is to collect “fingerprints” from elements in similar compounds and to identify common features<sup>2</sup>. The aim of this work is to identify modifications of metal nitrides and carbides by different ELNES. Metal nitrides are found in many systems of technical interest, e.g. as precipitates in steels or as hard coatings on cutting and shaping tools.

In order to relate the fine structures directly with atomic structure features, experimental ELNES-spectra are compared with band structure calculations of chromium nitride (CrN) and dichromium nitride (Cr<sub>2</sub>N). CrN is paramagnetic with NaCl structure (fcc). Cr<sub>2</sub>N consists of hcp Cr with N in the octahedral interstices. Both powders (purity >99%) were supplied by Alfa Aesar<sup>®</sup>. For the EELS-measurements they were crushed in an agate mortar, dispersed in ethanol and placed on a holey carbon grid.

Experimental work was carried out on a 200 kV Philips CM20 TEM with a LaB<sub>6</sub>-cathode, equipped with a Gatan Imaging Filter, with a measured energy resolution of 0.7 eV at full width half maximum of the zero loss peak.

The spectra were calculated with the TELNES module of the Wien97 code<sup>3</sup>. The calculation was done without taking magnetism into account and without spin-polarization. The instrumental broadening was modelled by a Gaussian of FWHM 1.5 eV and the excited lifetime broadening was approximated by an energy-dependent Lorentzian broadening of FWHM 0.1xE with E energy above the edge onset.

Fig.1 shows the measured N K edge of CrN together with the results of the bandstructure calculation. Features in the experimental spectrum match the theoretical ones, although with lower energy resolution. The ELNES of the hexagonal Cr<sub>2</sub>N phase exhibits a completely different ELNES; only one sharp peak and a broad shoulder are visible, which are accurately predicted in the calculated N K edge.

The differences between the fine structures of the N K edge in CrN and Cr<sub>2</sub>N can be explained by the differences in the local environment of the Cr and N in the two materials. In CrN, chromium is in an octahedral environment leading to e<sub>g</sub>/t<sub>2g</sub> splitting of the d orbitals. The structure labelled A (figure 1) is mainly due to hybridisations between N 2p and Cr 3d e<sub>g</sub> states (the t<sub>2g</sub> are occupied) while the structure labelled B is due to hybridisation between N 2p and Cr 4s. In Cr<sub>2</sub>N, Cr are surrounded by only 3 N atoms and there the d band is not split. Because the ELNES of Cr<sub>2</sub>N and CrN differ considerably even at the energy resolution of 0.7 eV, these fine structures can be used as a means for distinguishing between the two compounds. Recently, similar ELNES fingerprints have been found for the isostructural vanadium nitrides (VN and V<sub>2</sub>N)<sup>4</sup> thus suggesting that the findings of this study can probably be extended to other isostructural binary compounds (MX and M<sub>2</sub>X; M = transition metal and X = C,N,O).

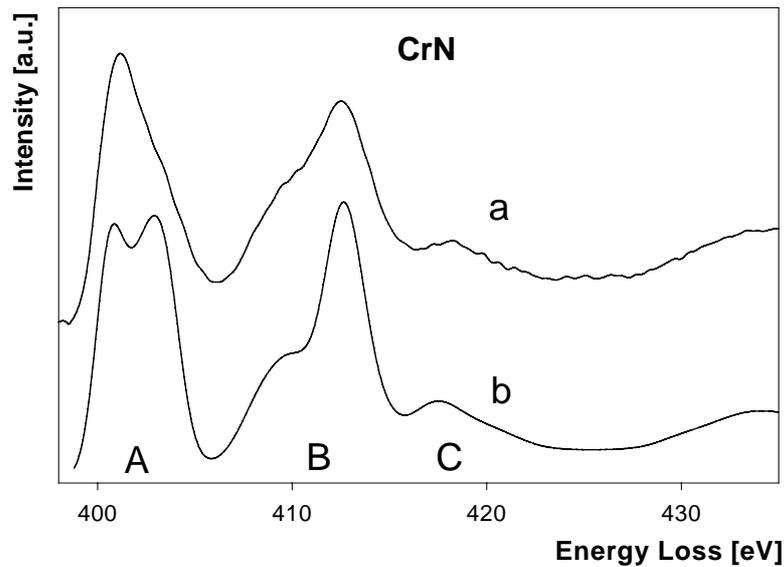


Figure 1. N K edge of CrN, comparison of experimental edge (a) with the calculated edge (b) (Wien97, 1.5 eV + lifetime broadening).

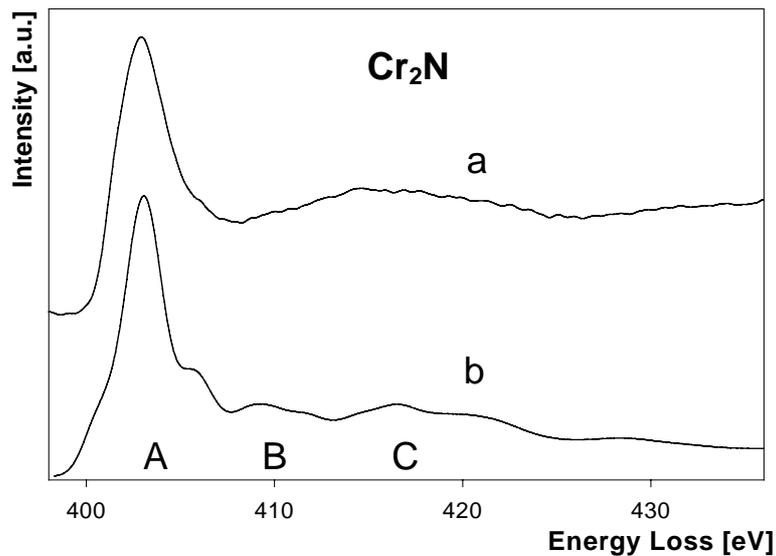


Figure 2. N K edge of Cr<sub>2</sub>N; experimental edge (a) compared with the calculated edge (b) (Wien97, 1.5 eV + lifetime broadening).

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## AEM Investigation of Strontium Substituted La-Co-Perovskites

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Due to their high ionic conductivity strontium-substituted lanthanum cobaltites ( $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ) have potential applications as solid oxide fuel cell cathodes, gas separation membranes or oxygen sensors. In the heavily Sr doped materials, the ionic conductivity obtained from galvanostatic polarization experiments shows a distinct maximum at certain values [1]. This behavior at high oxygen non-stoichiometry may be explained by oxygen vacancy ordering thus decreasing the mobility of the vacancies [2].

In order to confirm the assumption of vacancy ordering, two powders with  $x = 0.6$  and different oxygen concentrations are investigated by TEM: LSC ( $3-\delta \approx 3$ ) and LSC+ ( $3-\delta = 2.71$ ). LSC was annealed at  $1400^\circ\text{C}$  and slowly cooled to room temperature to yield near-stoichiometric composition. The higher oxygen vacancy concentration in LSC+ was reached by equilibrating the annealed material at  $p(\text{O}_2) = 10^{-3}$  bar for 60 h at  $825^\circ\text{C}$  and subsequent quenching to room temperature.

Looking at the elemental distributions, EFTEM reveals that both samples are perfectly homogenous at a nanometer scale [3]. The bright field image of LSC+ in Fig. 1a shows a single particle with a typical domain structure, i.e. bright and dark regions, which is not found in LSC. The dimension of these domains is between 50 and 200 nm. The electron diffraction pattern along the  $[4\ 2\ -1]$  zone axis (hexagonal description) shows additional reflections which originate from these two sets of domains (Fig. 1b, see arrows). The extra spots may be explained by a superstructure. In order to resolve a possible difference between the two domains, HRTEM images of the domain boundary of LSC+ particles in the same orientation are acquired (Fig. 2). The insets in the HRTEM image are Fourier transforms (FFTs) of two adjacent domains, which are rotated about  $90^\circ$  (in the image plane) with respect to each other and exhibit a doubling of the lattice spacing. These spatially resolved superstructure spots (arrows in Fig. 2) correspond to the extra spots in the SAED pattern (Fig. 1b). The near-edge fine structure of the oxygen K ionization edge looks significantly different for both samples (Fig. 3), which agrees well with the assumption that the superstructure is due to the ordering of oxygen vacancies thus changing the chemical surrounding of the oxygen atoms.

By these AEM investigations the occurrence of a superstructure in LSC+ is confirmed, which is presumably due to the ordering of oxygen vacancies. This ordering is responsible for the decrease of the ionic conductivity with increasing oxygen vacancy concentration.

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- [4] We gratefully acknowledge financial support by the *Fonds zur Förderung der wissenschaftlichen Forschung, Austria* within the Special Research Program *Electroactive Materials*.

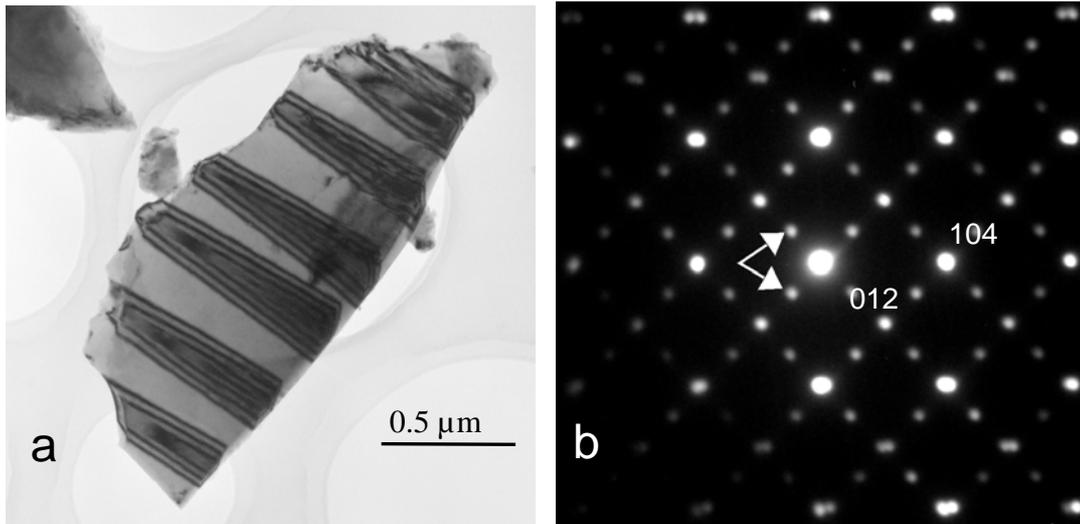


Fig. 1a. TEM bright field image of LSC+, b. SAED pattern with superstructure spots (see arrows) in [4 2 -1] orientation (hexagonal indexing).

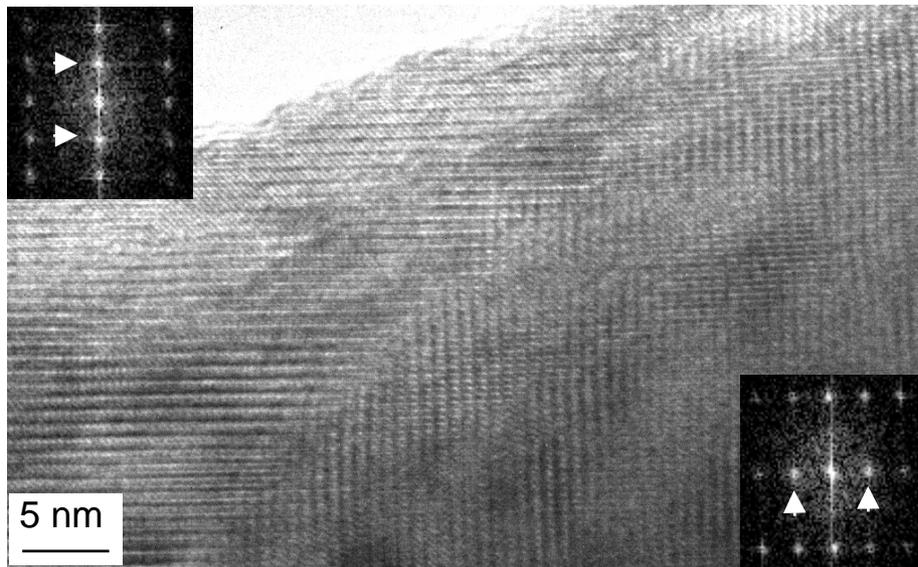


Fig. 2. HRTEM image of an LSC+ particle, showing two domains rotated about 90° with respect to each other. The insets show the corresponding FFTs; spots due to superstructure are marked.

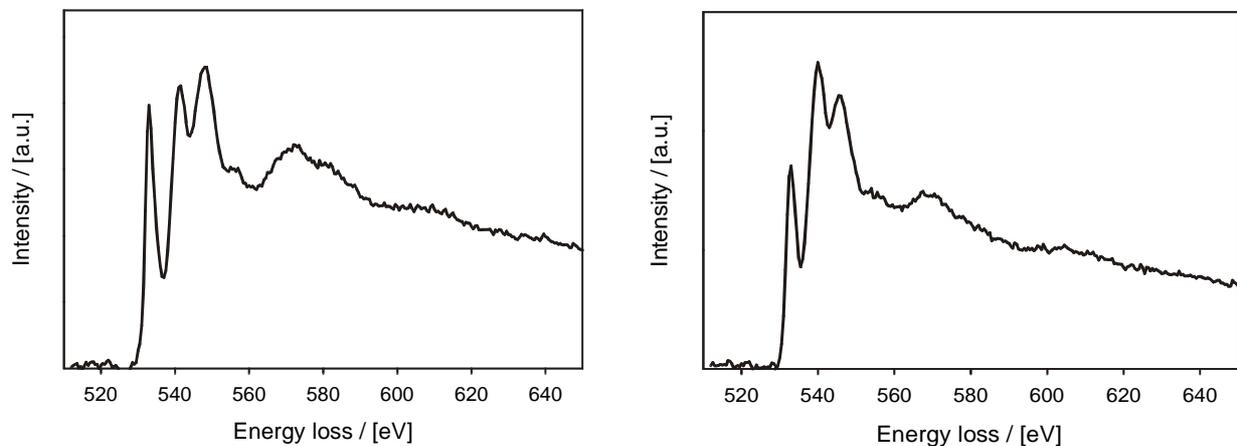


Fig. 3. Near-edge fine structure of the O K ionization edge of LSC (left) and LSC+ (right).

## Seasonal- and Age-Dependent Changes of the Structure and Chemical Composition of the Spherites in the Midgut Gland of the Harvestmen *Gyas annulatus* (Opiliones)

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Spherites, concentrically layered cytoplasmic inclusions, are most commonly found in the digestive, storage and excretory tissues of different phyla, e. g. Mollusca, Crustacea, Aranea and Insecta [1,2]. Spherites are described to contribute to the hardening of the exoskeleton and detoxification processes in studied arthropods [1,2].

The aim of this study was to find out if there are seasonal- and age-dependent changes in the structure and chemical composition of spherites in the midgut gland of the harvestmen *Gyas annulatus*. Knowledge about the changes of spherites during the life cycle of *Gyas* could elucidate their biological importance in this group (Opiliones), which was until now almost unknown.

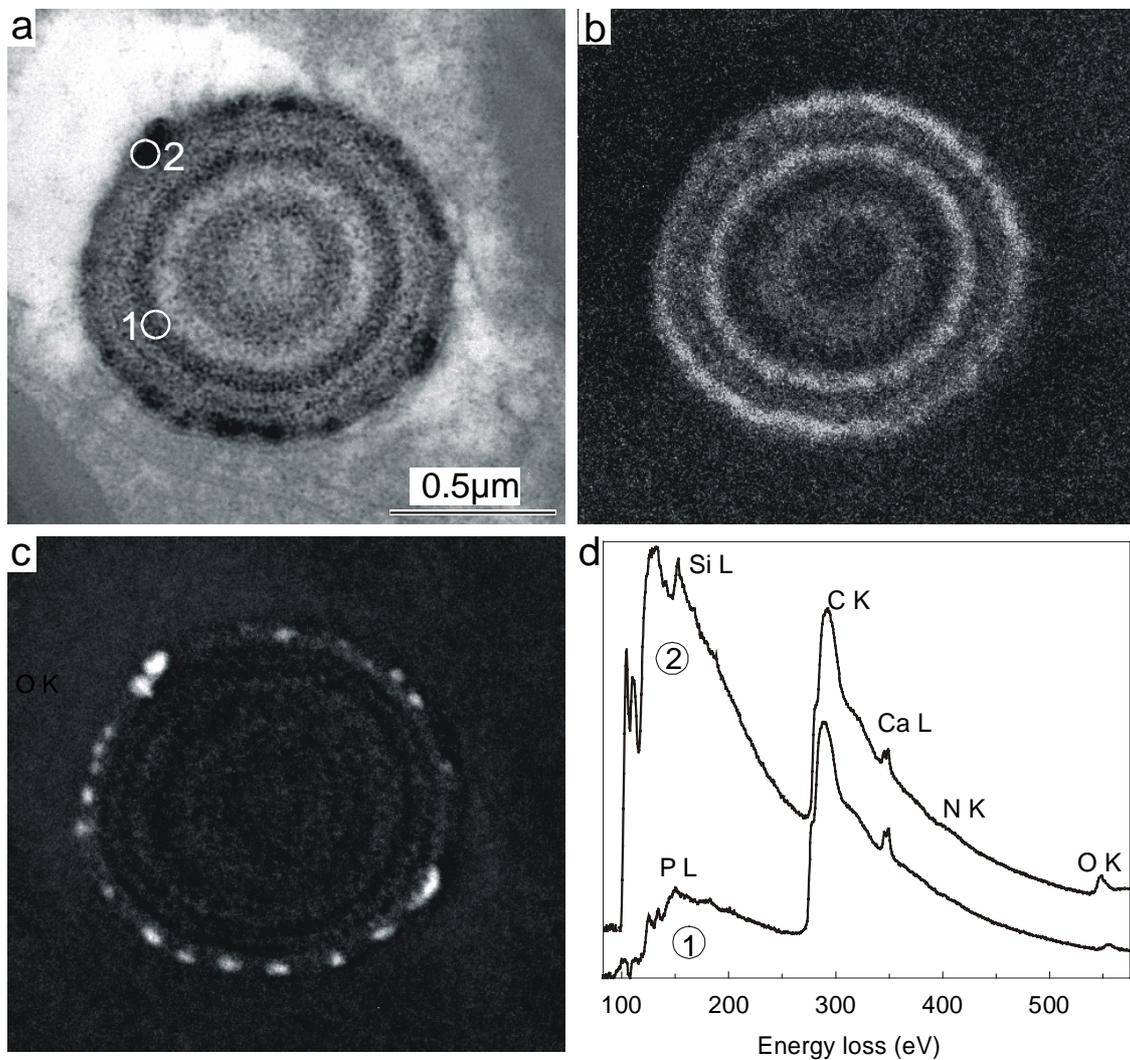
The spherites, located in the midgut gland of *Gyas* consist of an organic matrix composed of glycoproteins and proteoglycans whose sugar portion are carboxylated glycosaminoglycans. Different elements are embedded in this matrix, and their presence varies during the life cycle. All spherites in juveniles are composed of alternating concentrically arranged electron dense and electron lucent layers of organic matrix material before overwintering (December). The chemical composition of the spherites was characterized by a combination of electron energy-loss spectroscopy (EELS) and energy filtering TEM (EFTEM) [3,4]. In December, spherites contain calcium, phosphorus and silicon. Calcium and phosphorus are located in their electron dense layers, and silicon spotwise, mainly peripheral (Fig.1). Material seems to be lost during overwintering of *Gyas* as electron lucent „empty“ layers appear in spherites in March. The „lost“ material could be used as energy supply and/or to provide molecules for synthesis processes during non-nourishing overwintering. Spherites do not contain calcium and phosphorus in July and October. These elements seem to have important biological relevance in the formation and hardening of the cuticle during the moultings in spring. In contrast to calcium and phosphorus, silicon is still stored in spherites in July and October but in decreasing concentration, therefore it could be involved in metabolic processes in adult *Gyas*. In the period from July to the end of their adult life in late autumn, an increasing number of spherites disintegrate and their remnant organic matrix material progressively aggregates with other cellular waste material in one or more huge vacuoles of glandular cells.

The results presented in this study constitute the first report of the seasonal- and age-dependent structural changes of spherites in the harvestmen *Gyas annulatus*. The finding of calcium and phosphorus storage in the digestive system of *Gyas* is consistent with previous reports on the content of spherites in other animals [1,2,5]. Silicon was previously only found in the spherites of an additional harvestmen, namely *Phalangium opilio* [5] and as there is almost no silicon in spherites of *Gyas annulatus* containing only one electron dense layer, just before their assembling into the big vacuole, silicon could be used for some metabolic processes in Opiliones.

The combined application of TEM, EELS and EFTEM methods [6] in the study of spherites in *Gyas* is advantageous in comparison to previously applied methods. Most of the histochemical methods and EDXS used in previous studies of the spherites provided only an overview of their chemical composition. The EELS-spectra obtained in our study provide the first detailed description of the chemical composition of spherites. Using EFTEM we recorded additional information about the spatial distribution of different elements within the spherites at nanometer resolution. Our combined use of analytical electron microscopy methods provides both an overall as well as detailed characterization of the elemental composition of spherites in different stages of the *Gyas* life cycle.

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**Fig. 1:** Ultrathin section of the midgut gland from the harvestmen *Gyas* caught before overwintering (December). **a)** Bright-field TEM image of a spherite. **b)** Ca map, recorded with the Ca L<sub>2,3</sub> ionization edge. **c)** Si map, recorded with the Si L<sub>2,3</sub> ionization edge reveals silicon rich granula. **d)** EELS-spectra of Ca containing layer (curve 1) and of Si rich grains (curve 2) (spectra were taken from the regions marked in Fig. 1a).

## Nano-Particles in Aluminum Alloys Improve the Mechanical Properties

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Aluminum materials are characterized by their low density with at the same time very good mechanical properties. The mechanical characteristics can be significantly increased by an aimed heat treatment [1]. The heat treatment consists of solution heat treating, quenching and aging. With the solution heat treatment nearly the liquidus temperature and following quenching in cold or warm water a supersaturated solid solution is produced [2]. That means in the metal lattice are more foreign atoms solved than in the equilibrium phase corresponding to room temperature. The following aging at elevated temperatures leads to precipitates (so called Guinier Preston zones) in the metal lattice because of diffusion. The size of these precipitates is in the nanometer-range and depends on the heat treatment parameters. The kind (coherent or incoherent) and size of the precipitates affect significantly the increasing of mechanical properties.

In a co-operation project between the Research Institute for Electron Microscopy (FELMI) and the Austrian Foundry Institute (OGI) the nano-precipitates at different heat treatment parameters have been investigated. Two samples of the alloy G-AlSi<sub>7</sub>Mg<sub>0.6</sub> were cast and heat treated with the following parameters:

	<b>Solution</b>	<b>Quenching</b>	<b>Aging</b>
<b>T6</b>	535°C / 5h	Water / 70°C	165°C / 5h
<b>T7</b>	535°C / 5h	Water / 70°C	200°C / 5h

The T6-heat treatment leads to highest strength with lower elongation, however the T7-heat treatment (so-called aging) leads by coagulation of the precipitates to highest elongation but with lower strength. An advantage of the T7- heat treatment is, that in the practical use of the castings at elevated temperatures no changes of mechanical properties and measures arises because the microstructure is nearly the equilibrium condition.

For optimization of the material properties it is necessary to understand the nano-structural precipitation arising during the heat treatment. Therefore investigations with electron microscopic methods are very well suitable.

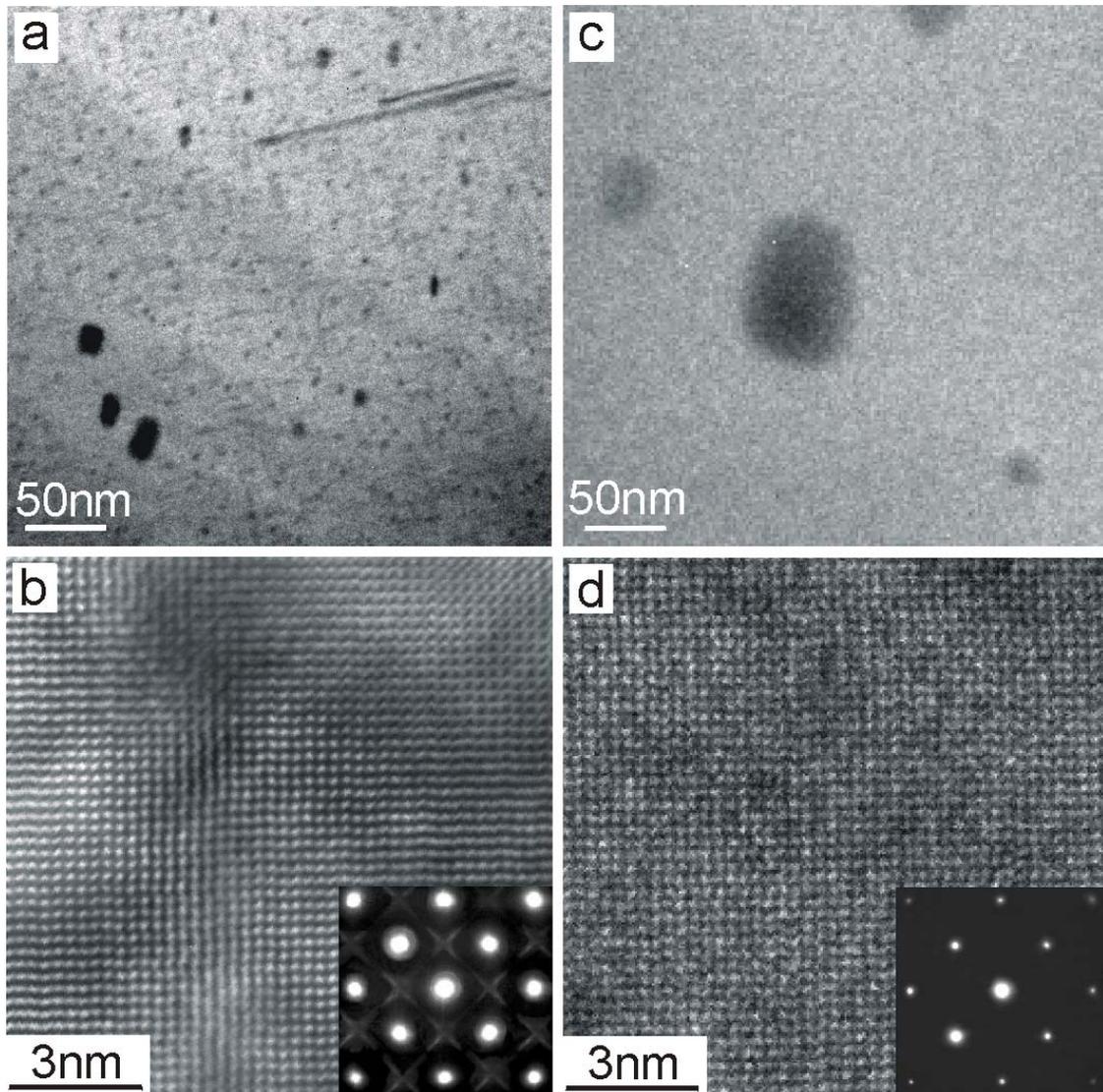
The TEM investigations were performed with an analytical high resolution electron microscope TECNAI F20, equipped with a field emission gun and a high resolution imaging filter. With energy filtering transmission electron microscopy (EFTEM), high resolution microscopy (HRTEM) and electron diffraction (SAED) we investigated the microstructure of samples T6 and T7. The aluminum distribution map of sample T6 (Fig. 1a) shows besides some larger particles a huge amount of very small precipitates with 1-2 nm in size (Guinier-Preston-zones) whereas in sample T7 (Fig. 1c) only a few large particles are visible (precipitates are indicated as dark regions in the elemental distribution maps as the concentration of the correspondent element is less there than in the surrounding matrix). The Guinier-Preston-zones of sample T6 (visible as coherent phases in the HRTEM image Fig. 1b) cause additional cross-like reflections between the matrix reflections in the

diffraction pattern because of their small dimensions (inset of Fig. 1b). As expected for the Guinier-Preston-zone free sample T7 the atoms are arranged more regularly (Fig. 1d) and the diffraction pattern does not show any additional reflections.

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*Co-operation project between the Center for Electron Microscopy (ZFE) and the Austrian Foundry Institute (OGI), supported by the Federal Ministry for economic affairs and labour*



**Fig. 1:** a) and c) show aluminum distribution maps of sample T6 (a) and sample T7 (c): the small precipitates (1-2 nm) in sample T6 (dark regions) are not present in sample T7. The slightly bent atom rows in the HRTEM image of sample T6 (b) indicate the presence of G.-P.-zones, which results in streak-shaped additional reflections in the SAED pattern (inset). Without G.-P.-zones (sample T7) the lattice planes are more regularly and the SAED pattern shows only matrix reflections (d).

## Transition Metal Oxide Doped Mesostructured Silica Films

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Mixed metal oxide materials such as silica-titania, silica-zirconia, etc. are of importance for a variety of applications, including sensors and catalysts. However, despite the great interest in these materials, their synthesis is still a challenging task. Not only a good accessibility, high dispersion and homogeneous distribution combined with a high loading of the transition metal oxides is required, but for many applications a deliberate design of porosity is also necessary. Moreover, the processing in a controlled morphology is a prerequisite, since not only powders but porous *thin films* are of special interest, e.g. for sensor applications. The typical synthetic routes towards porous mixed metal oxide catalysts e.g. titanosilicalites [1] or mesostructured silica-titania mixed oxides such as hydrothermal Si/Ti co-precipitation or postsynthetic grafting are not viable for the synthesis of thin films because either phase separation occurs due to the different hydrolysis and condensation rates of the various precursor alkoxides or only low loadings can be achieved (Si:Ti = 50:1).[2,3]

In this study, well-ordered mesostructured silica-transition metal oxide films with a high loading of the transition metal up to a Si:M (M = Zr, Ta, Ti) ratio of 5:1 and a good dispersion of the metal in the silica pore wall is presented. The preparative route we have chosen is based on a modification of polyethylene glycol-containing surfactant molecules with transition metal alkoxides. These novel surfactants are used in the synthesis of mesostructured silica-titania mixed metal oxide thin films serving different functions: a) as moderator of the hydrolysis rate of the transition metal alkoxide, b) as structure-directing agent, and c) for a deliberate positioning of the transition metal oxide species within the silica matrix (avoiding phase separation).[4]

The addition of this transition metal alkoxide modified template molecule resulted in a stable sol in which no precipitation of transition metal oxide species was observed, thus indicating, that the hydrolysis and condensation rate of the transition metal alkoxide is sufficiently retarded.

The major question, whether the novel modified surfactant still acts as structure-directing agent with lyotropic properties was investigated by X-ray diffraction studies (fig. 1a) and TEM (fig. 1b). The X-ray diffraction patterns clearly show reflections, which can be associated to repeating unit distances of 3.7-3.1 nm for the different samples. However, because of the orientation of the films, no clear indexation of the repeating unit to a hexagonal, cubic or lamellar phase is possible. TEM can be applied to visualize the mesophases in the thin films. Figure 2 shows the TEM images for Ti- and Zr-doped samples corresponding to the XRD-patterns. For the silica-titania based film, clearly the typical fingerprint pattern of a hexagonal mesostructure (fig. 2a-b) can be observed with a repeating unit distance corresponding well to the one obtained from XRD. For the zirconia-doped sample a striped pattern with a repeating distance of approx. 2.5 nm is clearly visible in the image (fig. 2c). This distance is not compatible with the repeating unit distance obtained from the X-ray diffraction pattern, however, it might as well be, that the image in the TEM is tilted and thus no correct distance is measurable. Both techniques, however, show that the modified surfactant still shows lyotropic properties, resulting in nicely ordered mixed metal oxide materials.

EELS was used to quantify the composition of the final film with respect to its Si/M atomic ratio (fig. 3). It was found, that the elemental composition of the films corresponds very well to the nominal composition (precursors in the starting solution (Si:Ti = 15:1)), thus indicating, that the transition metal oxide species is well-dispersed in the silica matrix which was also supported by XPS analysis.

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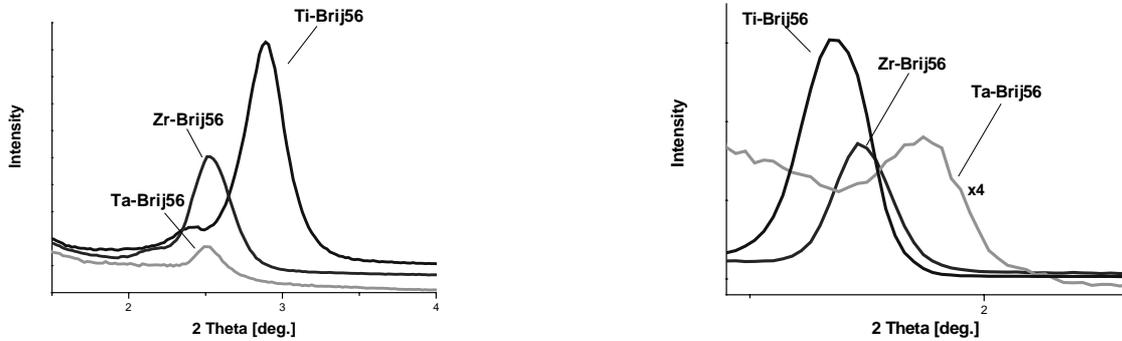


Fig.1a: XRD patterns of M-doped films, as coated on the left side, calcined on the right side.

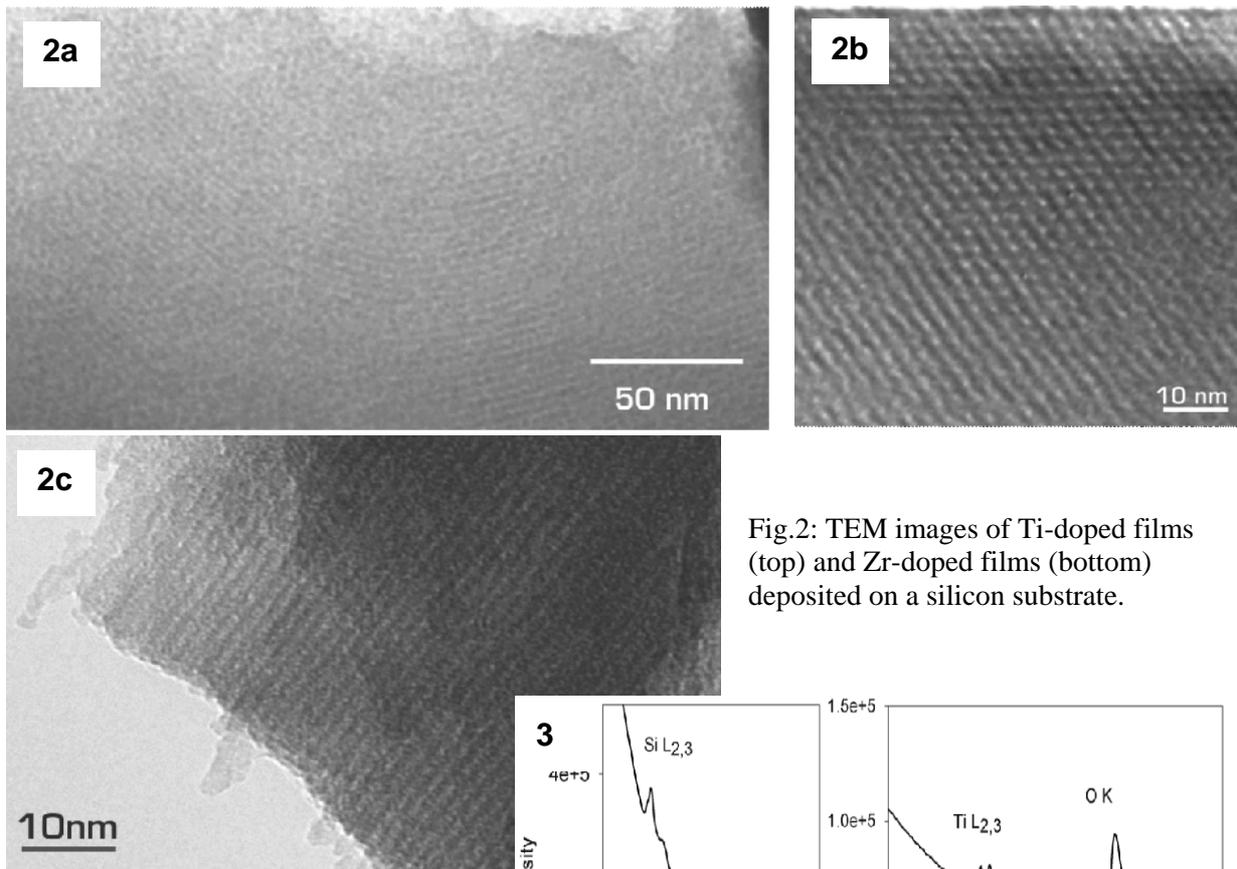
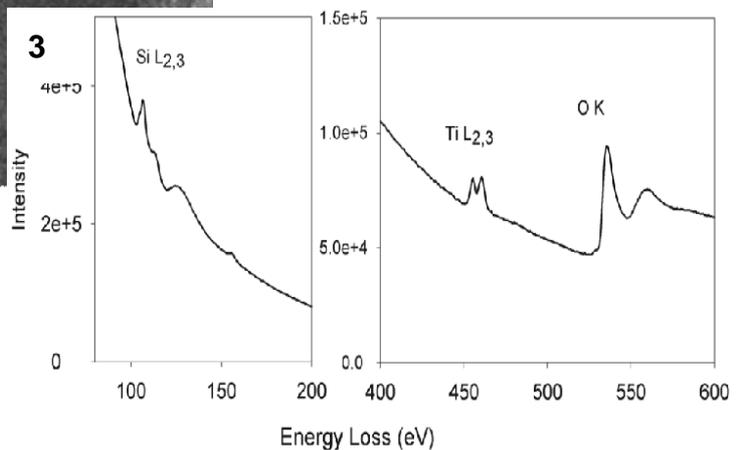


Fig.2: TEM images of Ti-doped films (top) and Zr-doped films (bottom) deposited on a silicon substrate.

Fig. 3:  
 EELS spectrum of a Ti-doped film,  
 Quantitative analysis gives 34 at% Si,  
 2.5 at% Ti and 63.4 % O.



## Ultrastructure of Pyrenoids in Green Algal Taxonomy

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Together with photosynthetic pigments and storage products the structure of plastids (or chloroplasts) plays an important role in the taxonomy of eucaryotic algae. The basic structures of algal plastids consist of membranous envelopes and membraneous vesicles (*thylakoids*, containing the chlorophylls) surrounded by a matrix or stroma that may or not may be traversed by thylakoids [1]. In many representatives of the most algal classes but very frequently in the green algae (chlorophyta) dense differentiated regions within the chloroplast occur and are designated as *pyrenoids*, a term first used by Schmitz 1882 [2, 3]. Although the pyrenoids of eucaryotic algae are varied in morphology the stroma always consists of proteinaceous material with granular appearance (sometimes paracrystalline, fig.1)[4].

A number of morphological types of pyrenoids exists [2,5] which are species-specific especially when their morphology and location can be used as a reliable diagnostic feature [6, 7, 8, 9,10].

In most members of the green algae an existing pyrenoid is embedded in a starch- containing chloroplast and frequently associated with the storage product itself by forming a characteristic starch sheath. This starch sheath can be composed of two or few large starch segments (figs.2, 6) or may consist of many small grains (fig.1). The matrix of the pyrenoid can be homogenous or penetrated or even traversed by thylakoids (figs.3, 4). Sometimes tubular or ramified invaginations into the matrix appear (fig.5). Among diagnostic features for identifying green algal species with light microscope the pyrenoid with its starch components should accurately be studied, using staining procedures as described [8,11]. When algal cells and their pyrenoids are difficult to observe according to their insignificance, successful confirmation of a pyrenoid's existence has to be done with TEM microscopy. As an example the pyrenoid in the chloroplasts of *Stichococcus* ssp. (green algae, Trebouxiophyceae) is sometimes difficult to see with light microscope and species with and without pyrenoid are cited [12]. But with TEM a distinct pyrenoid was observed in the chloroplasts of the most common species *Stichococcus bacillaris* NÄG. [13,14] (fig.3). The pyrenoid in the closely related taxon *Diplosphaera chodatii* BIALOSUKNIA corresponds with the type in *Stichococcus* (fig.4). Pyrenoid ultrastructure was also reliable in the taxonomy of *Trebouxia* spp. (a common green algal symbiont in lichens, class Trebouxiophyceae). 8 groups of species were distinguished by arrangement and morphology of their thylakoids [7]. The pyrenoid of *Trebouxia showmanii* (HILDR.& AHMADJ.) GÄRTNER from the "gigantea" type with characteristic invaginations into the matrix and numerous pyrenoglobuli can be seen in fig.5.

Recently the investigation of 4 cultivated species of the green algal genus *Planophila* based on molecular data [15] showed a relation of the investigated taxa to 3 different algal classes. But also the very different ultrastructure of pyrenoids supports this splitting of a previously homogenous group. The characteristic pyrenoid of *Planophila laetevirens* GERNECK (the type species of the genus) with some invaginations into the matrix and the distinct starch sheath composed of few thick starch segments is seen in fig.6 [16]. There is no doubt that pyrenoid ultrastructure contributes enormously to the taxonomy of green algae (as well as to taxonomy of other algal classes) and should always be considered in classification research.

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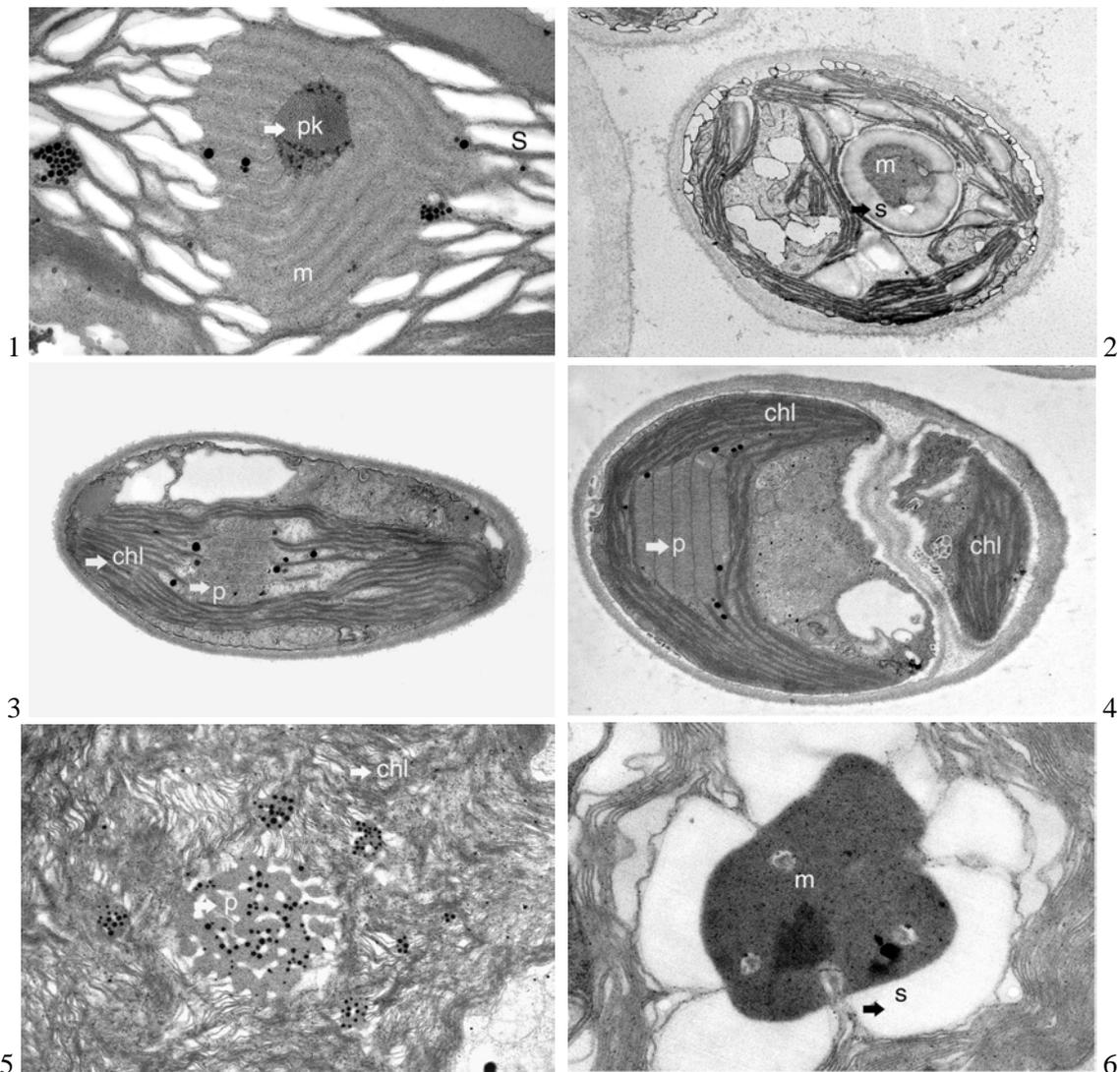


Fig.1-6 pyrenoid types of green algae:

1. *Chlorokybus atmophyticus* ( 16.566x ), para-crystalline matrix, lenticular starch grains.
  2. *Chlamydomonas gloeogama* ( 8.090x ), starch sheath of two segments.
  3. *Stichococcus bacillaris* ( 13.124x ), matrix traversed by thylakoids.
  4. *Diplospheera chodatii* ( 13.453x ), pyrenoid corresponds with 3.
  5. *Trebouxia showmanii* ( 9.090x ), invaginations into the matrix and numerous pyrenoglobuli.
  6. *Planophila laetevirens* ( 20.734x ), few invaginations into the matrix, starch sheath composed of few starch segments .
- s = starch, chl = chloroplast, p = pyrenoid, m = matrix, pk = para-crystalline part of matrix

## Establishment and Characterization of Human Medullary Thyroid Carcinoma – Cell Lines

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Medullary thyroid carcinoma (MTC) is a rare calcitonin - producing tumor of the parafollicular or C-cells of the thyroid. It accounts for 8 – 12% of all thyroid carcinomas. MTC may arise as a sporadic tumor or as a component of one of three autosomal dominantly inherited cancer syndromes: multiple endocrine neoplasia type 2A (MEN2A), type 2B (MEN2B), or familial MTC (FMTC). Mutations in the *ret* proto-oncogene were shown to be associated with MEN2. Presently, the only available cure for MTC is radical surgery. Prophylactic thyroidectomy is recommended for gene carriers before the age of five years. The early onset of metastases and the resistance of MTC to chemo- or radiation-therapy present further problems.

For almost two decades, only a single continuous MTC-cell line, TT, was available. Our aim was to establish further cell lines from MTCs, representing different tumor stages, growth dynamics, differentiation, ages of patients, and sporadic or hereditary forms. We collected tumor tissue samples from Austrian hospitals and set up cultures from 60 MTCs. Continuous cell lines could be established from nine specimens. The other 51 grew as cell lines with limited lifespans [1].

The cell lines were characterized and authenticated by cytogenetic, immunocytochemical and ultrastructural methods. Transmission- (TEM) electron microscopical preparations were made from 1) original tumor tissue (Fig.1.), 2) cultured cells from early (Fig. 2) and later times of cultivation (Fig.3-5), and 3) cultured cells which had been transplanted into nude mice (nu/nu- BALB/c) (Fig. 6). The presence and numbers of neurosecretory granules served as markers for the grade of differentiation. The original tissue was rich in granules (Fig. 1). These membrane-bound, highly electron-dense granules always decreased during cultivation, while the Golgi zones become prominently enlarged (Fig. 4, 5). The cells projected many short microvilli, indicating absorptive processes (Fig. 3). Transplantation of cultured cells into nude mice proved tumorigenicity. In addition, the number of granules was enhanced again, thus restoring their original differentiation and demonstrating the correlation with the tissue of origin (Fig.6.).

Our cell lines have a variety of applications: MTCs are well known for the phenomenon of *bcl-2*-based chemo- and radioresistance. An overexpression of the antiapoptotic gene *bcl-2* extends cell viability by blocking apoptotic cell death. For this reason, our aim is to modulate the proliferation, the viability and *bcl-2*- expression by treatment with new anticancer drugs or with factors that are known for their anticancer effects in other tumors. Our cell lines provide models for the study of growth dynamics, endocrine cell differentiation, cytogenetic properties, and tumor progression, they could be important models for the design and performance of future clinical trials for the treatment of MTC [2, 3].

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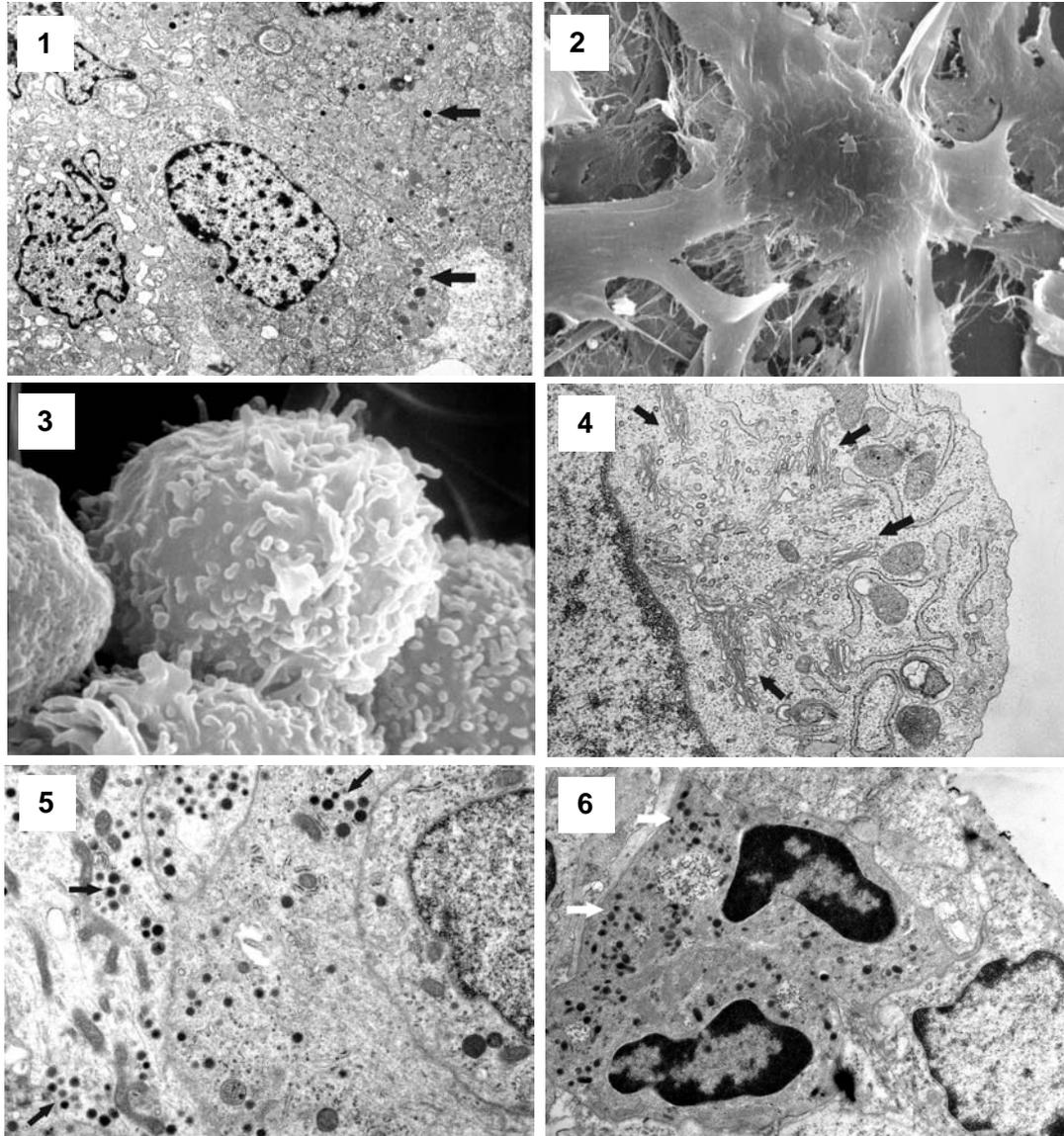


Fig.1. Medullary thyroid carcinoma, original tumor tissue with plentiful typical secretory granules (arrows) (TEM 4.146x)

Fig.2. Primary culture of the MTC-SK cell line. Multicellular aggregate, formed in a monolayer. Development of suspension culture (SEM 300x)

Fig.3. MTC-SK, a suspension culture of multicellular aggregates with numerous microvilli has developed (SEM 6.600x)

Fig.4. A single cell of the MTC-SK cell line after 21 passages. Only a few endocrine granules are present, while the Golgi zone is prominently enlarged (arrows) (TEM 11.220x)

Fig.5. Endocrine granules in another cell line, HST, after 11 passages (TEM 7.455x)

Fig.6. Tumorigenicity test of the MTC-SK cell line in nu/nu BALB c mice. The xenotransplant contains an increased number of endocrine granules (white arrows) (TEM 7.100 x)

## TEM Investigation of INCONEL 718 with Dark Field Imaging and High Resolution Transmission Electron Microscopy

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Inconel 718 is a nickel-base superalloy largely used in the fabrication of critical pieces for turbine engines because of its high mechanical properties as well as good corrosion resistance. In addition, this alloy can easily be forged and welded [1]. The strengthening phase in this alloy is the long, disk-shaped and metastable body-centered tetragonal  $\gamma''$ -phase ( $\text{Ni}_3\text{Nb}$ ). A smaller amount of  $\gamma'$ -phase  $\text{Ni}_3(\text{Ti},\text{Al})$  appears as fine dispersed, quasi-spherical particles, which are coherent with the matrix. Their strengthening effect is much smaller than that of  $\gamma''$ -phase[2]. According to literature [3]  $\gamma'$ - and  $\gamma''$ -precipitates are formed simultaneously in the temperature range 700°C to 900°C for short time aging. In this work we have been mainly interested in the study of the  $\gamma''$ -precipitation resulting from an isothermal aging performed after quenching.

Two samples of Inconel were at first heated at 1060°C for 2 hours and then, in order obtain different concentrations of precipitates, the samples A2 and A7 were kept at 720°C for 1 and 16 hours, respectively.

The TEM investigations were performed with an analytical high resolution electron microscope TECNAI F20, equipped with a field emission gun and a high resolution imaging filter. With energy filtering transmission electron microscopy (EFTEM), high resolution microscopy (HRTEM) and electron diffraction (SAED) we investigated the microstructure of samples A2 and A7.

Bright field observation of sample A7 aged at 720°C for 16 h shows a matrix with a uniform and very fine precipitation (fig.1a). The corresponding diffraction pattern (fig. 1b) shows spots of  $\langle 001 \rangle_\gamma$  zone axis of the matrix plus superlattice spots. One can distinguish two types of superlattice spots: the first are round shaped, some of them are being localized at half distance from the matrix spots, others being merged with them. Their identification shows that they belong to  $\gamma''$  phase. The dark field image in fig.1e is recorded in the light of this type of reflection (marked as reflection 3 in the SAED pattern b). The second type of reflections (No. 1 and 2 in the SAED pattern) are elongated and lie along the  $\langle 100 \rangle_\gamma$  and  $\langle 010 \rangle$  directions. They belong also to  $\gamma''$  phase and give the dark field images in c) and d). From the three dark field images it can be deduced that the disc shaped  $\gamma''$  phase precipitates appear in three directions perpendicular to each other.

Fig.2a shows the high resolution TEM image of sample A7. The inset is the corresponding fourier transformed image which gives the same information as the SAED pattern (fig.1b). The lattice planes in the HRTEM image of sample A2 (720°C, 1 h) are more regularly but the SAED pattern indicates already very weak extraspots which proves that although the short annealing time precipitation of  $\gamma''$  phase has already started.

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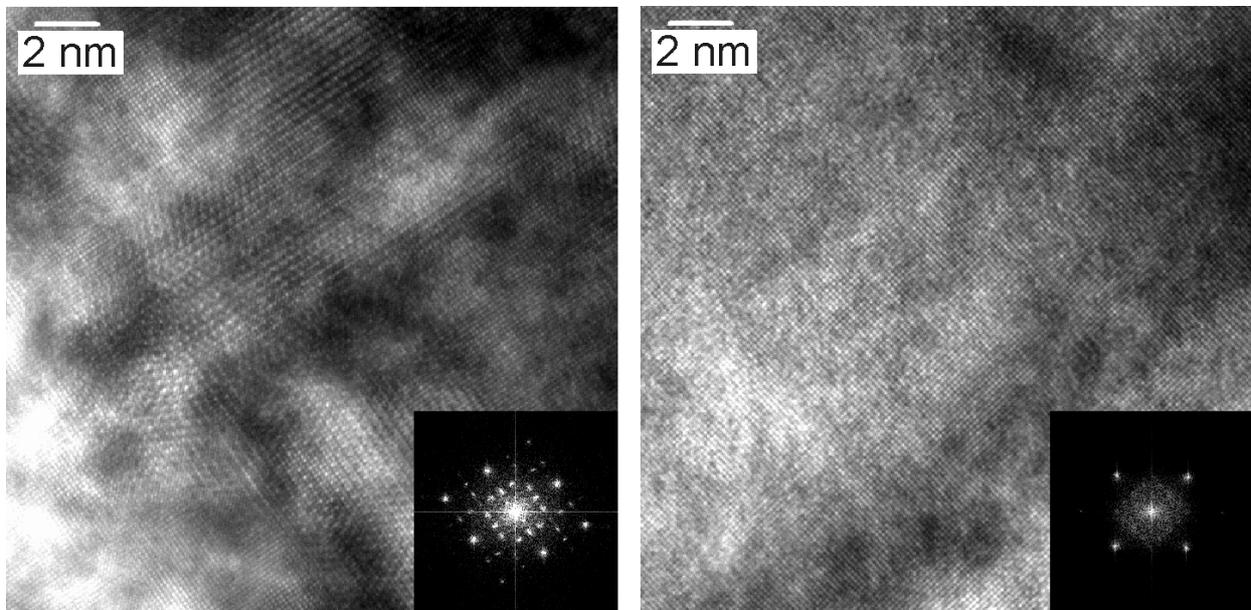
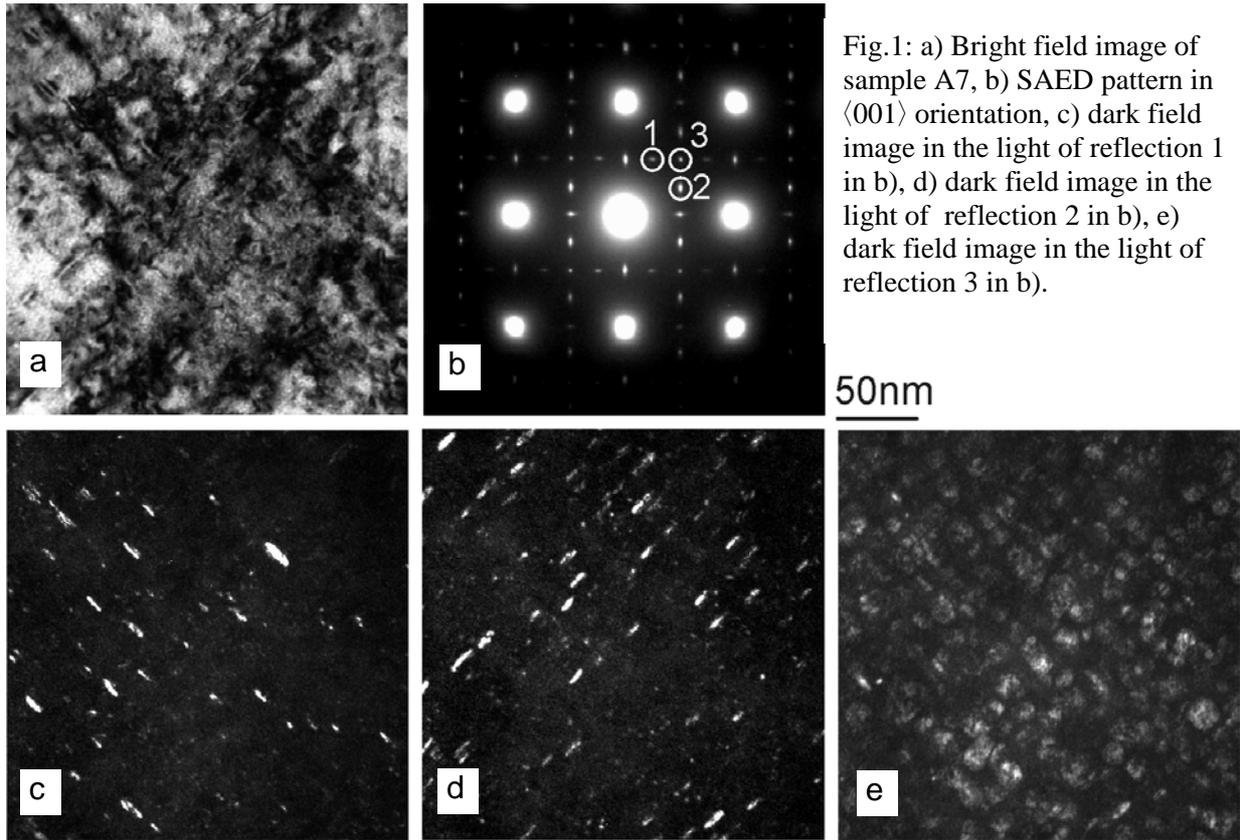


Fig.2: a. HRTEM image in  $\langle 001 \rangle$  orientation of sample A7, the inset is the Fourier transformed image showing additional reflections due to coherent  $\gamma''$  precipitates, b) HRTEM image in 001 orientation of sample A2, the fourier transformed image proves that precipitation has already started.

## Characterization of Precipitates in INCONEL Alloy using SAXS and TEM

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The shape, size and size distribution of precipitates decisively influence the macroscopic mechanical behavior of modern alloys. Though these materials represent a very important technological issue, the characterization of their structural properties in *nm* range is still not well established. Many metallic alloys are hardened by precipitates which are hindering the movement of dislocations in the material. Applying specific thermal treatment, which induces the nanometer sized precipitates, the properties of many alloys can be optimized. The purpose of this contribution is to demonstrate possibilities of small angle x-ray scattering (SAXS) in combination with transmission electron microscopy (TEM) for the characterization of an industrial superalloy. Inconel<sup>2</sup> 718 is a precipitation strengthened nickel-chromium base superalloy containing significant amounts of iron, niobium and molybdenum along with less amounts of aluminum and titanium. The studied Inconel specimen were homogenized for 2 hours at 1060°C and then annealed at 720°C for different times ranging up to 16 h.

SAXS:

The SAXS experiments were performed with the laboratory system NanoSTAR<sup>TM</sup> (Bruker AXS GmbH, Germany) with Cobalt radiation at 35 kV / 34 mA. Cross coupled Göbel mirrors, optimized for the CoK $\alpha$  wavelength ( $\lambda = 1.79 \text{ \AA}$ ), were used for monochromatization and beam collimation.

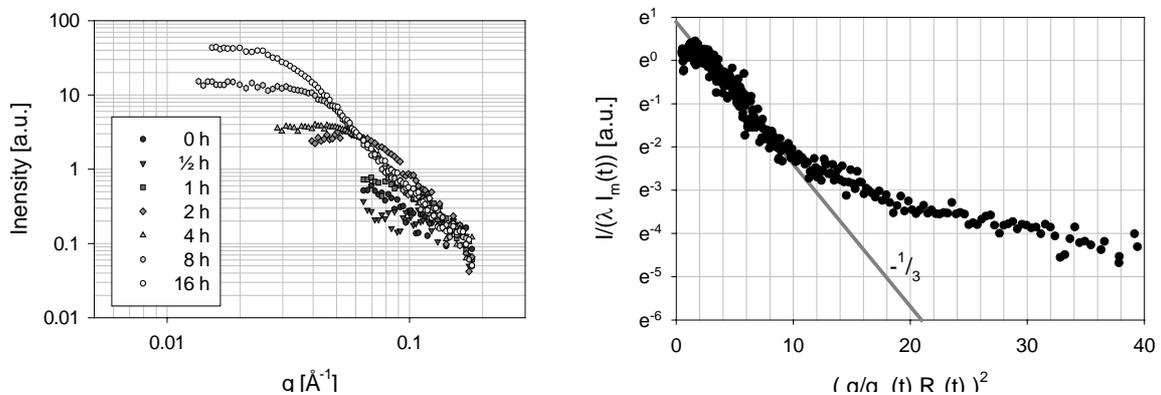


Fig. 1, left: Azimuthally averaged scattering intensity of Inconel. The samples were tempered for different durations as indicated in the legend. Right: Guinier Plot of the scaled profiles, according the scaling parameter  $q_m(t)$  and  $I_m(t)$ .

The background corrected SAXS data reveal a Porod regime in the lower  $q$ -range (around  $q \approx 0.01 \text{ \AA}^{-1}$ ). The scattering contribution of these relatively large particles was subtracted from the scattering curve, since these particles are not of main interest of the investigation. The resulting SAXS profiles exhibiting the time dependence of the scattering function are shown in Fig. 1. The maximum of the scattering intensity increase with annealing time and the peaks shift towards lower  $q$  - values in agreement with precipitate growth/coarsening. The scattering curves exhibit a scaling phenomena [1] during annealing. Two main parameters can be obtained from these SAXS experiments, particle size and mean distance between particles. For the former, the general form of the Guinier Law [2] was applied. Although the system is

<sup>2</sup> Inconel is a trademark of the INCO family of companies

not diluted, the straight part in the Guinier plot (Fig. 1, right) with a slope equal to  $-1/3$ , can be used to describe the size of scattering particles. Fig. 2, left, shows the radii of Gyration ( $R_g$ ) obtained from the scaled data. An estimate of the mean distance between the precipitates ( $D$ ) can be achieved from the scaled data using the relationship  $D=2\pi/(q/q_m(t))_{\max}$  (Fig. 2, right).

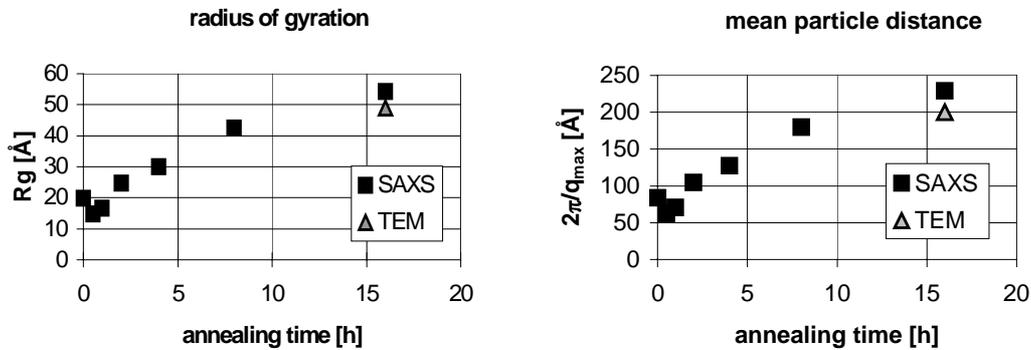


Fig. 2: Radius of Gyration (left) and the mean distance between the precipitates (right).

The TEM dark field images in Fig. 3 show the Inconel sample annealed for 16 h at  $720^\circ\text{C}$ . The micrographs clearly illustrates a plate-like shape. This is in agreement with the observed isotropic scattering in the 2D SAXS pattern. Estimating the average size of the precipitates directly from the TEM images and calculating the Radius of Gyration ( $R_g^2=d^2/8+h^2/12$ , with the diameter  $d$  and the height  $h$  of the disks [2]) a value of  $49 \text{ \AA}$  is obtained for this specimen. In comparison, the scattering techniques yield to  $54 \text{ \AA}$  (see Fig. 2, left). From an estimation of the mean distance between the disks out of the TEM images, a value of  $197 \text{ \AA}$  is obtained. This is in good agreement with the results obtained by the scattering technique (see Fig. 2, right). TEM investigations are suitable for the characterization of late stages of precipitation, where “large” particles have already been formed. Since for these specimen good agreement was found with the scattering technique, the results obtained from the latter for the early stages (with “small” precipitates) become more significant.

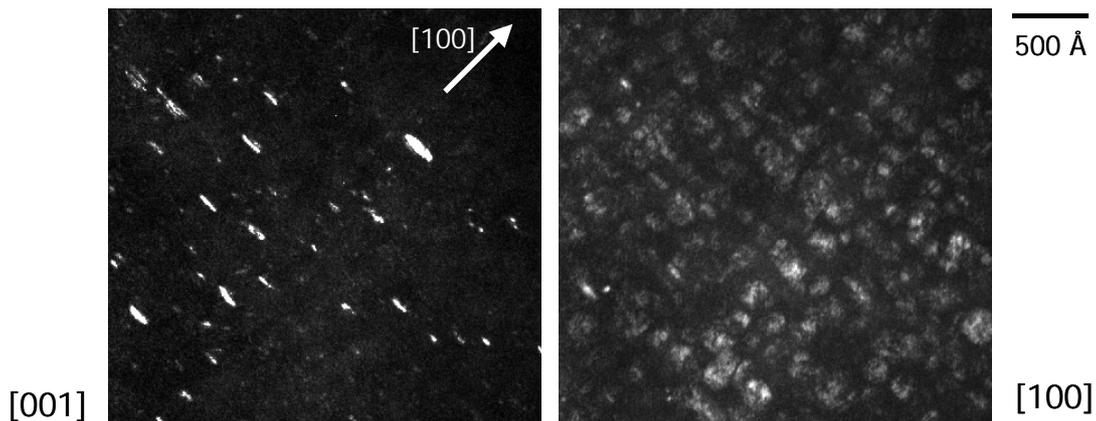


Fig. 3: TEM dark field micrographs of the Inconel sample annealed for 16 h at  $720^\circ\text{C}$  showing the presence of plate-like shaped precipitates.

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- Financial support of this work by the Technologie Impulse GmbH in the frame of the K-plus competence center program is acknowledged.

## Synthesis and Electron Microscope Investigation of Gold Nanocrystals

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Metallic nanoparticles are of interest in various scientific fields, e.g. optics, IR and Raman microscopy or for use in optoelectrical devices. The synthesis of gold and silver nanoparticles in aqueous and aqueous micellar solution is a common technique. In this work a seeding growth method has been used to prepare gold nanocrystals of controllable size and shape [1]. This seeding growth method is also suitable for other noble metals, e.g. silver nanorods and nanowires [2]. Major advantages of this technique are simplicity and low instrumental prerequisites.

The seed solution was prepared by adding 0.6 mL freshly prepared ice-cold aqueous 0.1M NaBH<sub>4</sub>-solution to 20mL aqueous 2.5×10<sup>-4</sup>M tetrachloroaurate/2.5×10<sup>-4</sup>M sodium citrate solution. The color changed immediately to a reddish brown indicating particle formation. The “growth-solution” was prepared in a conical flask using 2.5×10<sup>-4</sup>M tetrachloroaurate and 0.1m CTAB (cetyltrimethylammoniumbromide); afterwards 50μL freshly prepared aqueous 0.1M ascorbic acid solution was added to the growth solution. The solution was stirred, then 25μL seed solution was added. After gently shaking the flask, the reaction solution was let undisturbed, allowing the rods to grow. After several minutes the color of the solution slowly changed to pink, indicating particle growth. All reactions were performed at room temperature. After a reaction time of 3 hours the reaction solution was cleaned from the bulk of surfactant by centrifugating the solution at 5000 rpm, removing the supernatant and filling up the residue with distilled water. This procedure was repeated three times, whereas in the last step the residue was filled up with ethanol. TEM samples were prepared by treating the solution in an ultrasonic bath and putting some drops of the solution on a coated copper mesh grid. The TEM and HREM investigations were performed on a Philips EM420 and a FEI Tecnai F20 equipped with a field emission gun.

Fig. 1 shows representative overviews of the obtained nanocrystals. Several other crystal forms such as hexagonal plates were also present in the specimen, but the majority of the nanocrystals are small spheres and rods. It is interesting that the nanorods and -spheres are of very uniform size. The gold crystals seem to grow in the surfactant micelles present in the reaction solution and are obviously not able to grow beyond a certain size. The average particle size of the nanorods is 190 ± 20 nm length and 13.5 ± 0.2 nm diameter resulting in an aspect ratio ranging from 12 to 16.

HRTEM images of gold nanorods are shown in Fig. 2. The rod is orientated along the [110] zone axis. Preferred growth direction is the [100] crystallographic zone axis. The images show that there are stacking faults along the growth axis and, in addition, at least one twin plane in the center of the nanorod. This crystal defects are probably the main reason for the formation of nanorods. Detailed proposals for growth mechanisms of gold nanorods have been described by other groups, even an effort to describe all possible crystal structures of nanocrystals with cubic unit cell was made [3,4]. Furthermore, special attention was also devoted to gold nanotriangles, whereby the study of structural features of this particular crystal form is still in progress.

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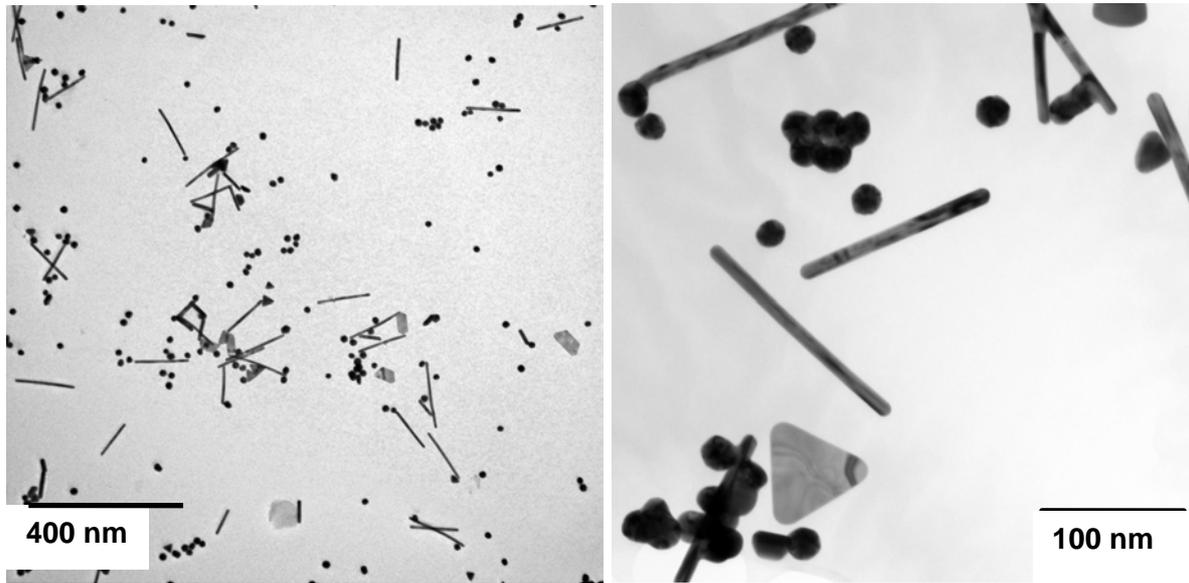
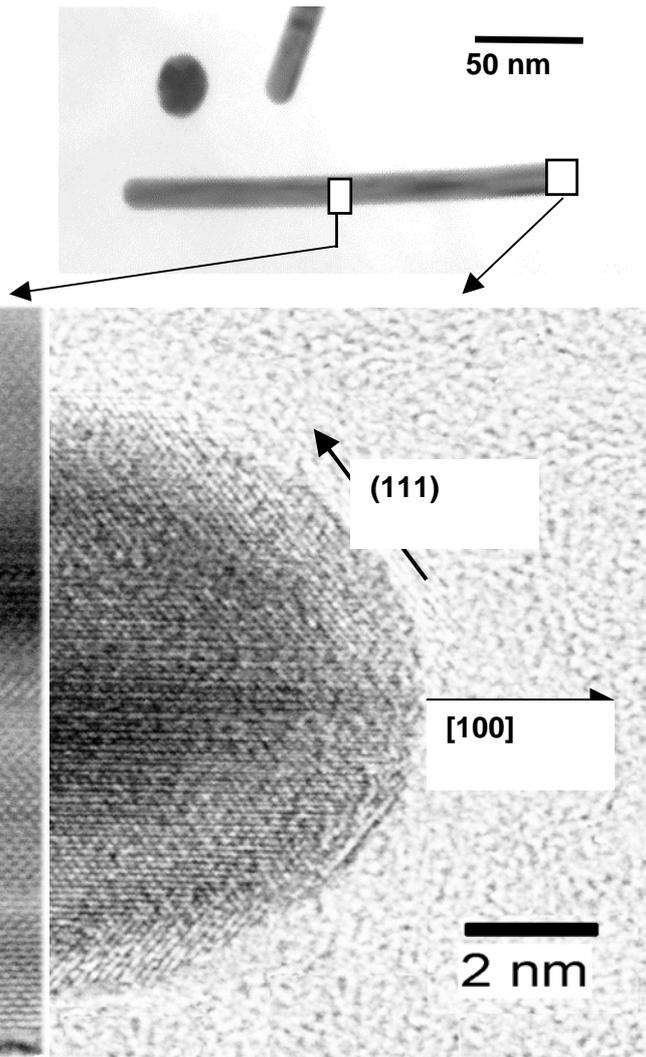


Fig. 1: TEM bright field images of gold nanocrystals grown with the seeding method

Fig.2: HRTEM images of single gold nanorod; twinning and stacking faults along the growth direction [100] are probably essential for the growth of the rods.



## HREM Study of Hexagonal and Rhombohedral Graphites for Use in Graphite Anodes in Lithium Ion Batteries

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It is well known that the performance of graphite for use as anode material in the lithium ion batteries largely depends on its bulk and surface structure [1]. It was, for instance, observed that the electrochemical behaviour is influenced by the graphite crystal modification. Layered graphite exists in two crystallographically different forms, the hexagonal form ( $\alpha$ - or 2H-phase) with a AB... graphene layer stacking sequence, and the rhombohedral modification ( $\beta$ - or 3R phase) with an ABC... stacking sequence [2].

In order to study the influence of the respective phases on the electrochemical behaviour, we have prepared and investigated two graphite samples: The first sample was prepared by heat treatment of graphite (courtesy of Superior Graphite Co.) at 2000°C under nitrogen gas to create 100%  $\alpha$ -phase. The second sample was made from the same graphite but mechanically processed by impact milling to increase the extent of the  $\beta$ -phase to about 25 %. The relative phase contents could be determined by x-ray diffraction [3].

HREM investigations in a FEI Tecnai F20 equipped with a field emission gun and a supertwin lens revealed very different surface and “sub-surface” morphologies for the two graphites. In case of the hexagonal graphite, unique convoluted graphene layers could be determined at the prismatic surfaces. If the crystal is viewed along the (001) zone axis, these layers are visible at the surface in the form of “lines” running parallel to the crystal edges (Fig.1a). A view along the (110) zone axis (Fig.1b) makes the convoluted “onion-like”-oriented graphene layers at the prismatic surface more clearly visible. An additional characteristic feature of this sample is the high stacking order in the sub-surface and bulk region. At contrast, the HREM-images of the rhombohedral graphite reveal disordered surface layers (Fig.2a) and a sub-surface region with many stacking faults and slight graphene layer bendings (Fig.2b).

The anode performance of these two graphite samples depends strongly on the electrolyte. It was found that differences in the sub-surface layer structure have a most significant influence on the performance in an ethylene carbonate/dimethyl carbonate-electrolyte. The differences in surface structure and morphology are considered to have the highest impact in a propylene carbonate/ethylene sulfite based electrolyte. Only for an ethylene carbonate/diethyl carbonate electrolyte, the performance differences are small [3]. Put it simply, the structural features of the respective graphites can be detected with a proper electrolyte.

As a simple rule, a high number of structural defects is beneficial to the performance; e.g. the discharge capacities are higher than those with hexagonal graphite. Additionally, these defects create hindrances inside the graphite, which just allow the small unsolvated lithium cations to penetrate into the bulk graphite. Therefore, the rhombohedral graphite is less vulnerable to co-intercalation of solvents, a reaction being detrimental to practical graphite anode performance.

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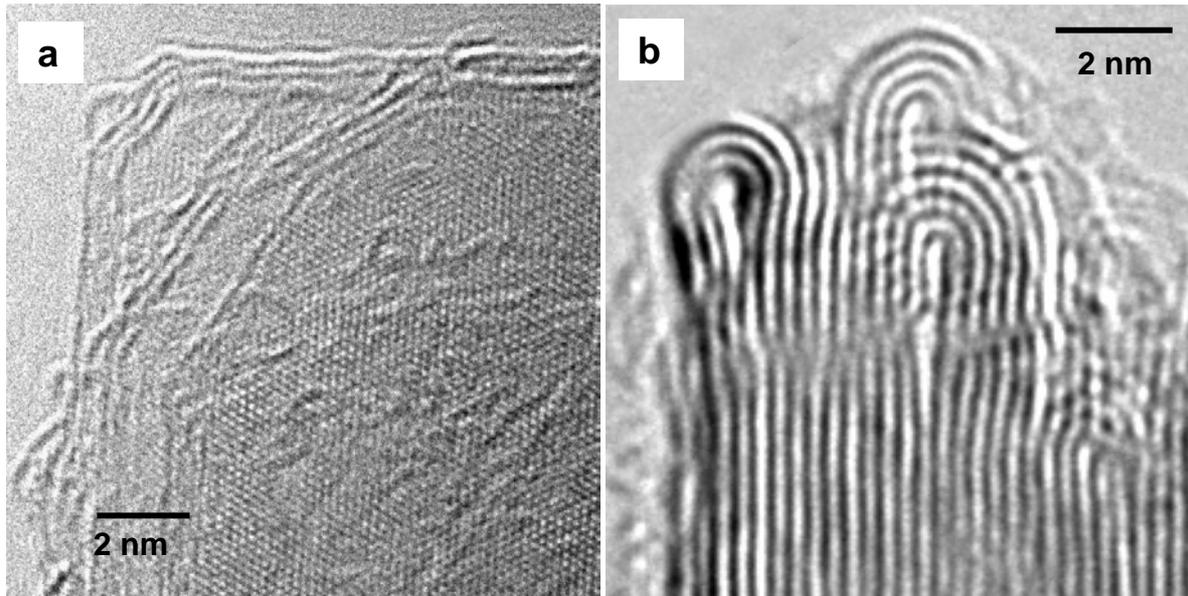


Fig.1 High resolution TEM image of hexagonal graphite heat treated at 2000°C under N<sub>2</sub>; a. crystal viewed along [001] zone axis; b. crystal viewed along [110] zone axis revealing the convoluted graphene layers at the termination of the prismatic layers.

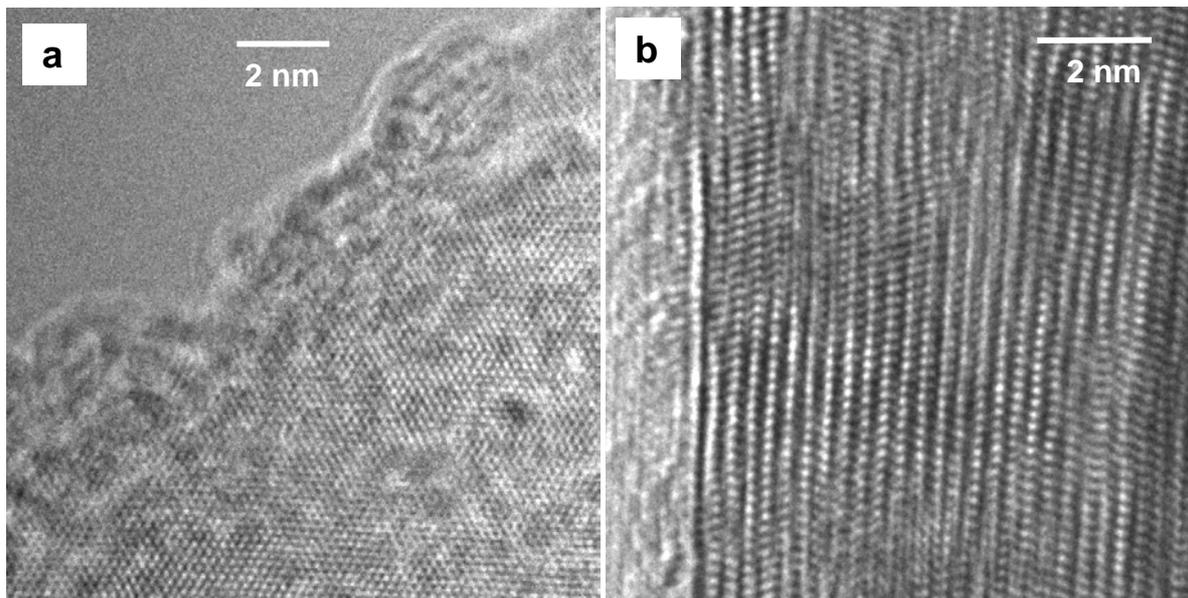


Fig.2 High resolution TEM image of rhombohedral graphite mechanically processed; a. crystal viewed along [001] zone axis; b. crystal viewed along [110] zone axis revealing the distorted graphene layers.

## Detection of Apoptotic Death of Vascular Smooth Muscle Cells by Transmission Electron Microscopy

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Arteriosclerosis is the primary cause of death in all western countries (1). The main risk factors for development of this disease are an elevated level of low density lipoproteins and oxidative stress. Interaction of oxidized low density lipoproteins with smooth muscle cells which are located in the media of the arterial wall represents a key process in atherogenesis. It may lead to apoptosis (programmed cell death) of smooth muscle cells which is a major event in the pathophysiology of atherosclerosis (2). Cells that are undergoing apoptosis exhibit characteristic changes in physiology as well as morphology (3). Morphological changes of an apoptotic cell include membrane blebbing, fragmentation of the nucleus, chromatin condensation and shrinkage of the cell volume. The best method to detect these changes is transmission electron microscopy.

The aim of this work was to investigate whether LDL that is only oxidized at its lipid part, so called minimally modified LDL (mmLDL), induces apoptosis of Human Arterial Smooth Muscle Cells (HASM). For this purpose cells were incubated with mmLDL for 8 hours, isolated and prefixed with glutaraldehyde in cacodylate buffer. After washing with cacodylate buffer, cells were fixed with 1 % osmium tetroxide in the same buffer, dehydrated by passing the samples through a series of ethanol solutions of increasing strength (30 -100 %) and embedded in Agar EPON 812. Ultrathin sections were prepared using a Leica Ultracut ultramicrotome, stained with uranyl acetate and lead citrate and viewed with a Philips EM 420 electron microscope.

Figure 1 shows the electron micrograph of a smooth muscle cell treated with mmLDL for 8 hours (left micrograph) in contrast to the untreated control cell (right micrograph). As shown in figure 1 treatment of human smooth muscle cells with minimally modified LDL resulted in morphological changes which are typical for apoptotic cell death such as membrane blebbing, fragmentation of the nucleus, chromatin condensation and a decrease of the cell volume. In contrast, membrane and nucleus were intact in the untreated control cell. Hence, these data provide clear evidence that minimally modified LDL leads to apoptosis of smooth muscle cells which is a detrimental process in the development of atherosclerosis.

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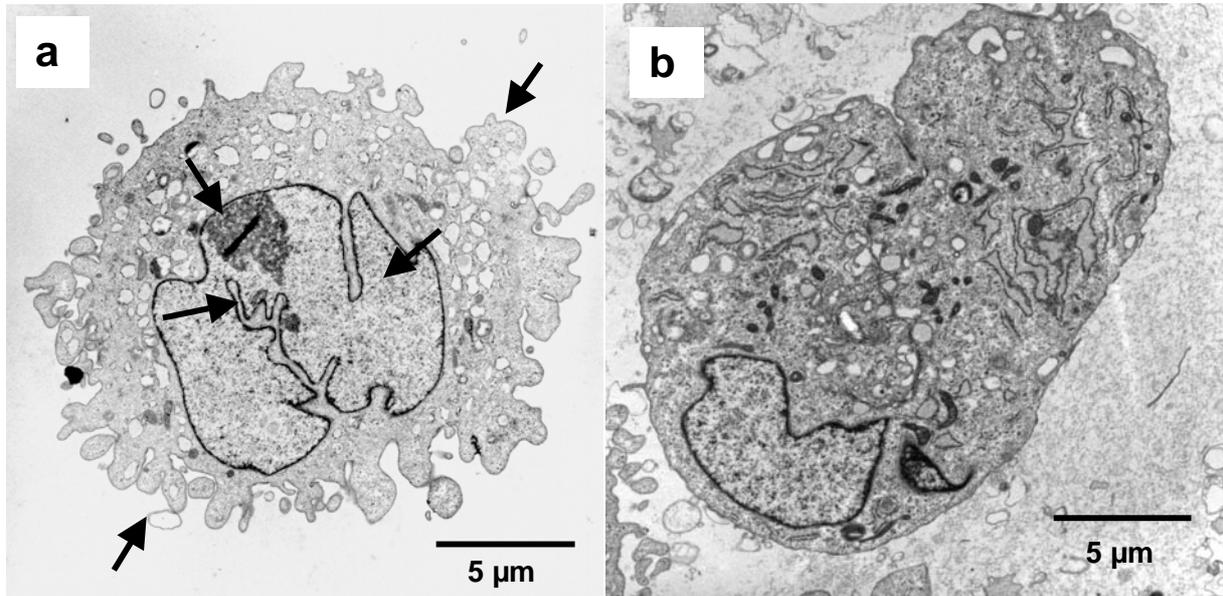


Fig. 1: Transmission electron micrographs of HASM. Effects of mmLDL on cell morphology.

Cells were incubated with (1A, left panel) or without mmLDL (control, 1B, right panel) for 8 hours, isolated and fixed by 3 % glutaraldehyde in 0,1 M cacodylate buffer for 1 day. After fixing, cells were washed, embedded and visualized by transmission electron microscopy with 6600 fold magnification. Changes in cell morphology after incubation with mmLDL as compared to the untreated control are indicated by black arrows.

## TEM Investigation of Greigites from Sediments of the Black Sea

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A sediment core from the deep basin near the continental slope of the Black Sea, the largest anoxic sea, C-193 ( 42°53,01'N and 29°10,0'E) from a water depth of 2040 m was analyzed for phase composition and biomineralization processes.

Samples of the sediment section from 15 to 80 cm were impregnated with synthetic resin and polished to be analysed by micro-probe X-ray diffractometry (Bruker Analytical X-Ray Systems) for mineral phases and by ore microscopy and electron microscopy for greigite (Fe<sub>3</sub>S<sub>4</sub>).

The sediment of the core consists mainly of transported minerals from the Danube like quartz, feldspar, clay minerals, calcite and dolomite as well as biologically induced minerals like magnesia calcite and aragonite. Additional phases like coccolithic calcite and framboidal greigite are formed by biologically controlled mineralization. The extraction of framboidal greigite from the sediment was done with a strong permanent Co-Sm magnet from water suspension of sediments. The water suspension was passed through a polyethylene tube squeezed by two strong Co-Sm magnets.

In order to visualize the greigites directly in the sediment, the resin embedded sample was cut with a diamond ultramicrotome and investigated in the Philips CM20 transmission electron microscope. Fig.1 shows the TEM image of a typical aggregate consisting of black particles with an average diameter of 250 nm. Convergent beam electron diffraction (CBED) was used to investigate the crystallography of single particles clearly revealing that the particles are really single crystals (fig.2a) and x-ray spectrometry (EDXS) showed that the particles consist mainly of iron and sulfide (fig.2b). Comparison with electron diffraction patterns from literature [1] and the quantification of the EDX-spectrum confirm that the black particles visible in the TEM image are greigite single crystals.

Framboidal greigite has formed at the border of oxic/anoxic zone in the Black Sea through the action of sulfate reducing bacteria [2], ever since highly saline sulphate-rich Mediterranean sea-water began to flow via the Bosphorus into the Black Sea. For about 9000 years the increase of the number of framboidal greigites in sediment is therefore correlated with its increasing sulfate content through the water-influx from the Mediterranean Sea [3].

### Acknowledgements:

We would like to thank Dr. E. Ingolic for ultramicrotome cutting of the sediment samples.

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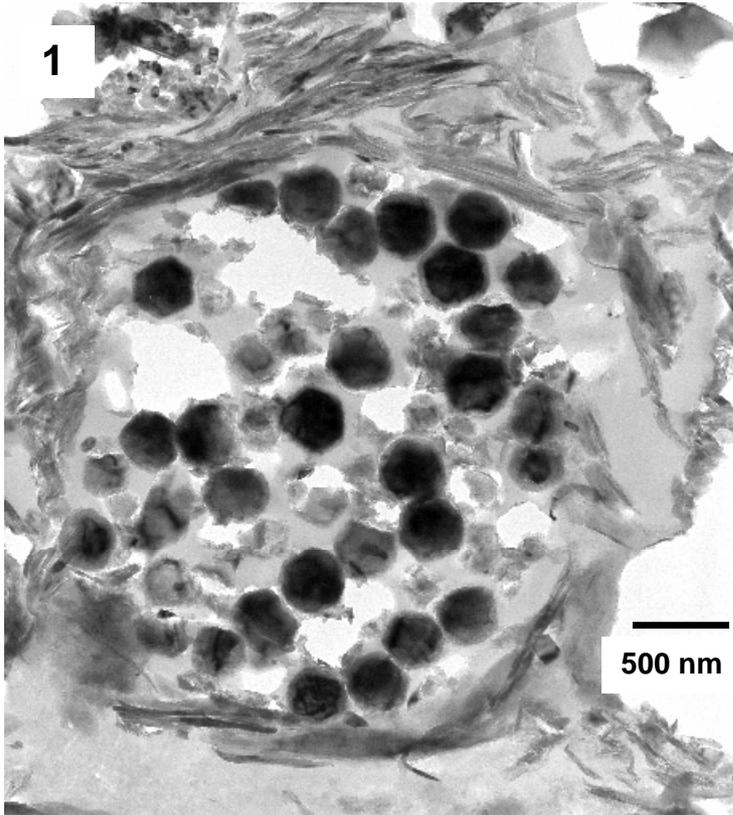


Fig.1  
TEM bright field image of  
framboidal greigite of the Black  
Sea, ultramicrotome section.

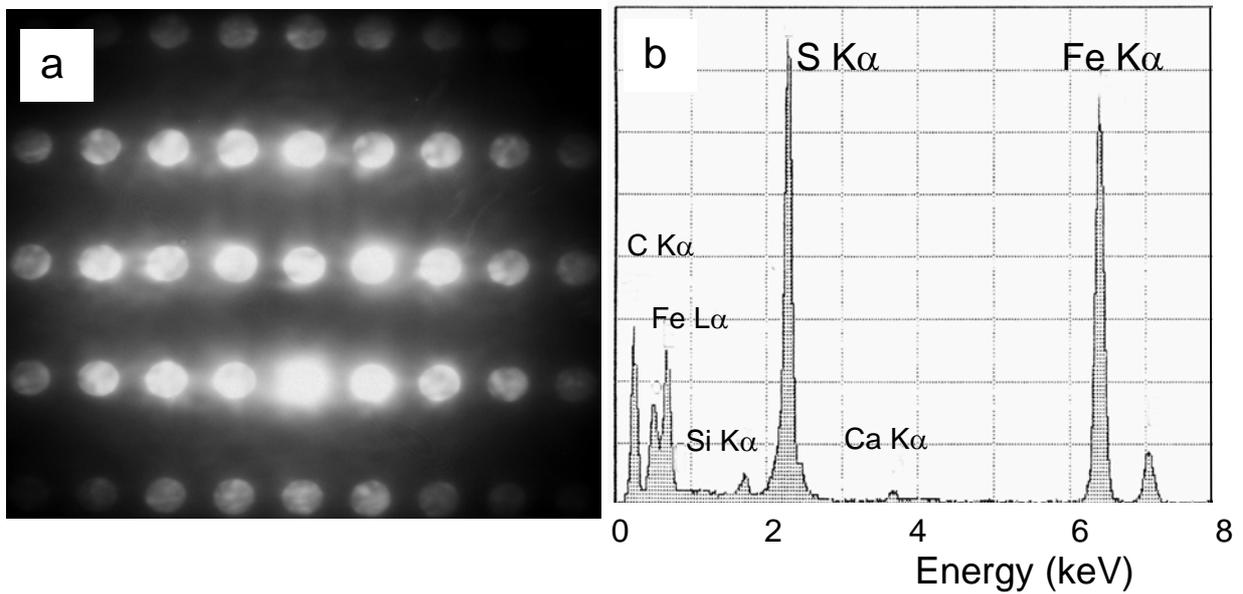


Fig.2: Characterization of the black particles from figure 1; a. Convergent beam electron diffraction (CBED) from a single greigite particle with beam parallel to the  $\{112\}$  zone axis; b. EDX-analysis.

## Characterization of the Interface Between Molybdenum Sealing Foil and Vitreous Silica by Energy-Filtering TEM

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In the lamp industry, the composite vitreous silica / molybdenum foil is of special importance. A composite that withstands higher operation temperatures and longer operation times can be created by applying molybdenum foils with a knife shaped edge doped with yttria and ceria [1]. Recently, tests with titania doped sealing foils have resulted in a higher stability under cyclic conditions, but results tended to depend on the sealing time. In order to explain this effect, it was suggested that the different behaviour of Ti- and Y-Ce-mixed oxide dispersoids during the sealing process could be caused by a difference in the distribution of the relevant elements in the composite interface.

Energy-filtering transmission electron microscopy (EFTEM) was employed to study the molybdenum / silica interface of three types of lamps produced with decreasing sealing time from lamp A to B to C. Molybdenum sealing foils doped with 0.52 wt% TiO<sub>2</sub> and 0.55 wt% Y-Ce-mixed oxide were analyzed before and after sealing with vitreous silica. The samples have been prepared in the form of TEM cross-sections employing low-angle ion milling.

Investigations of the interface region between the vitreous silica and the Mo-foil doped with titania revealed differences between the lamp types with respect to the distribution and concentration of the dopant. Auger electron spectroscopy (AES) was used to measure the titanium concentration on the surface of the mechanically separated foils [1]. For lamp C the titanium surface concentration is higher by a factor of 2 compared to lamp A which means that a longer sealing time leads to a lower titanium concentration in the interfacial region.

In order to study the titanium distribution in the interface region we have recorded energy-filtered TEM images which have been used to calculate jump ratio images with the Ti L<sub>2,3</sub> ionization edge [2,3]. In case of lamp A titanium is homogeneously distributed in the vitreous silica forming spherical particles with sizes of a few nanometers (fig.1b). However, for lamp C we find less titanium rich particles in the vitreous silica, but a local enrichment of titanium in the interface between the molybdenum ribbon and the silica (fig.2b) which is in agreement with the AES measurements.

Consequently, it can be concluded that the titanium rich oxide layer is a prerequisite for a chemical bonding between the partners, metal and glass, over the whole surface of the foil. In addition a correlation between the spatial distribution of the dopants and the joining-time could be established.

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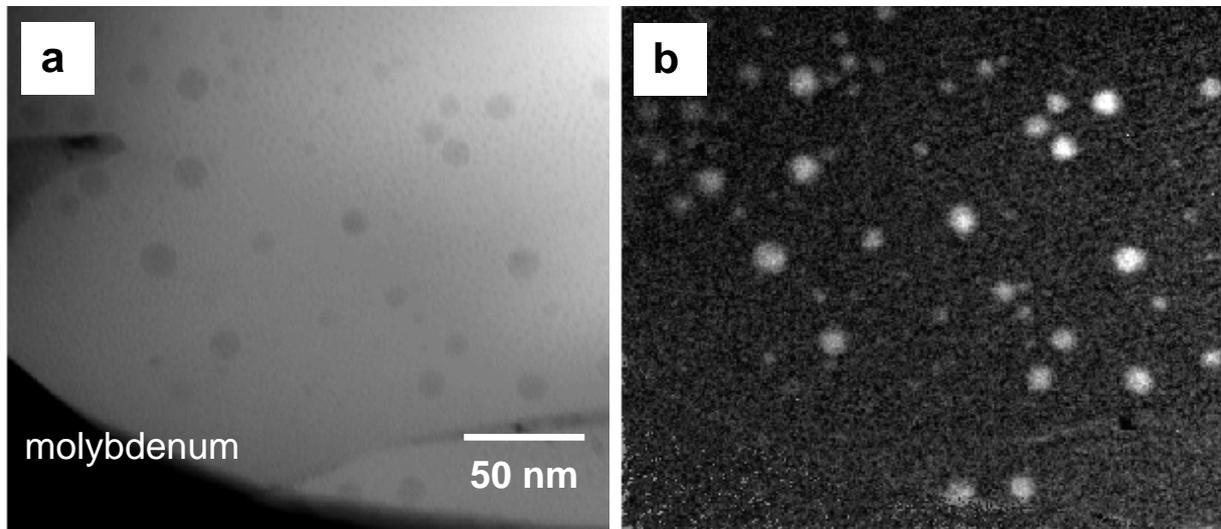


Fig.1 EFTEM investigation of the interface region of lamp A (longer sealing time); a. TEM bright field image; b. titanium jump ratio image recorded with the Ti L<sub>2,3</sub> edge.

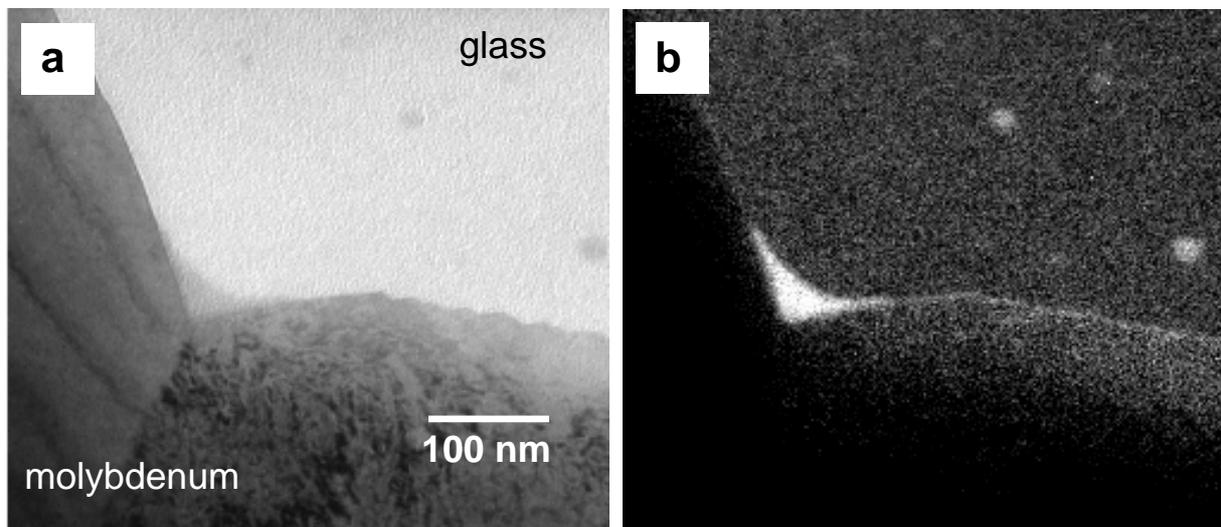


Fig.2 EFTEM investigation of the interface region of lamp C (shorter sealing time); a. TEM bright field image; b. titanium jump ratio image recorded with the Ti L<sub>2,3</sub> edge.

## Electron Microscope Characterization of Diesel Exhaust Particles

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In the discussion concerning air quality the airborne particulate matter is generally assessed to pose health risks. Epidemiologic and toxicologic studies indicate that inhaled fine particles get in the deep of the lung and effect the respiratory tract. However, airborne particulate matter is a broad class of chemically and physically diverse substances that exist as discrete particles (liquid droplets or solids) over a wide range of sizes from nanometers to about 100 micrometers [1], and not all of them are a health risk.

One important source of fine particulate matter is the emission of internal combustion engines, especially Diesel engines. So far the particulate matter of the Diesel engine emission is more or less assessed by the integral mass determined via filter sampling or exhaust opacity. Consequently, investigations to get a better understanding of particulate related parameters, such as surface, morphology, number size and chemistry are important. All the necessary information can be efficiently achieved by means a double differential mobility particle spectrometer (DDMPS) [2] and a transmission electron microscope (TEM). The combination of these techniques allows to access correlations between size and morphology and between the size number distribution [3].

The particulate matter of a Diesel engine was collected in the exhaust line using TEM grids covered with ultrathin (3-5 nm) carbon or chromium films in order to minimize the substrate contribution to the image. Special attention was devoted to reduce the influence on the sampling of the Diesel exhaust particles. In order to “freeze” the thermodynamic conditions the aerosol was diluted by using particulate free compressed air. The actual particulate collection on the TEM grid was realized by using a sampling device utilising separation by thermophoretic effect. The TEM investigations were performed with a Philips CM20 operated at 200 kV and equipped with an LaB<sub>6</sub> source. Elemental analysis was done with an energy-dispersive x-ray spectrometer (Noran HPGc).

A wide range of particle sizes, shapes and opacities are observed in the TEM images of the Diesel exhaust particles as shown in figures 1 and 2. Depending on the combustion conditions the morphology varies from complex branching aggregates consisting of small nanoparticles over relatively unstructured matter containing even nanotubular particles to samples consisting of mainly single nanoparticles. In most cases the typical soot particles consist of aggregates built of thousands primary particles which exhibit spherical shapes with diameters ranging from 10 to 30 nm (figs.1a-b). The linear extension of the aggregates is many times larger than the measured “electrical mobility diameter” which can vary between 50 and 200 nm. It was also found that the composition and the particle size distribution depends sensitively on the sampling of the particles.

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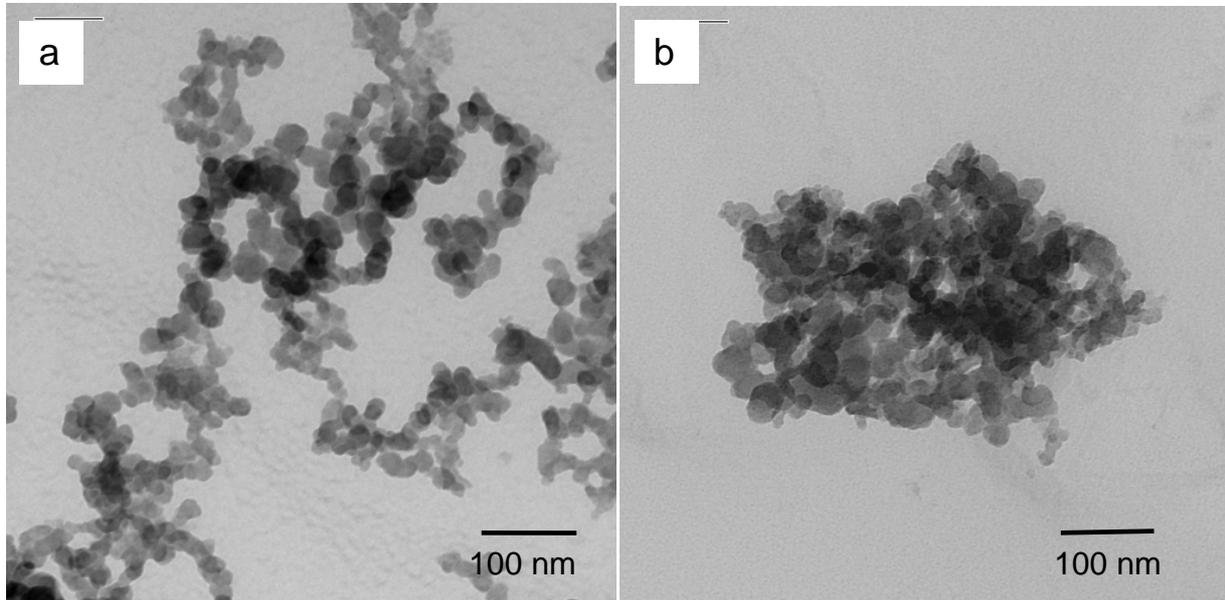


Fig.1 TEM-images of soot particles collected from  
a. sample of the electrical mobility size class 100 nm with an engine speed 1800 rpm, 2 bar BEMP  
b. sample of the electrical mobility size class 75 nm with an engine speed 1500 rpm, 1.9 bar BEMP.

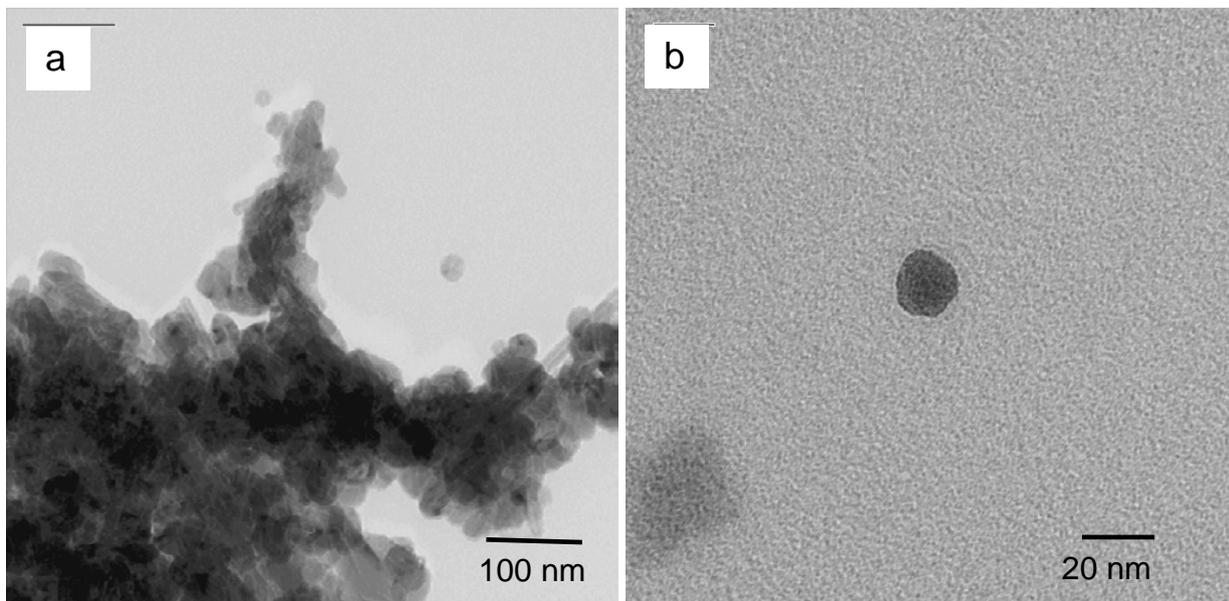


Fig.2 TEM images of soot particles collected from  
a. sample of the electrical mobility size class 15 nm with an engine speed 1500 rpm, 1.9 bar BEMP  
b. sample of the electrical mobility size class 15 nm with an engine speed 1500 rpm, 1.9 bar BEMP.

## Non-Centric Ion-Milling for Achieving Better TEM-Specimens

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The use of transmission electron microscopy (TEM) to support process development of advanced materials and microelectronic devices is often challenged by the difficulty of preparing thin samples from the bulk. In the last two decades ion-milling techniques emerged as the favorite method for preparing thin samples for TEM investigation. The only major disadvantage has always been, that the volume under study in the TEM is relatively small, making it difficult to get a representative view of the specimen. Therefore, increasing the area of the thinned region by ion-milling is critical in order to provide representative TEM results. This problem has been somewhat alleviated by the introduction of ion-milling under a low angle [1,2,3].

TEM specimen preparation by ion-milling usually employs ion-guns accurately focussed to the central area of the mechanically pre-thinned region. This results in a specimen including a central hole with thin edges, where the high energy electrons can penetrate. Recently, we found that by directing the ion-beams to a region slightly displaced from the center of the disc, most of the beam will hit thicker areas of the specimen disk and ablation of specimen material will result in larger thinned areas. The pre-thinning of the sample was performed with a Gatan Dimple Grinder and ion-milling with a PIPS Ion-Polishing System (Gatan, Inc., USA). The TEM samples were investigated in a Philips CM20 TEM operated at 200 kV.

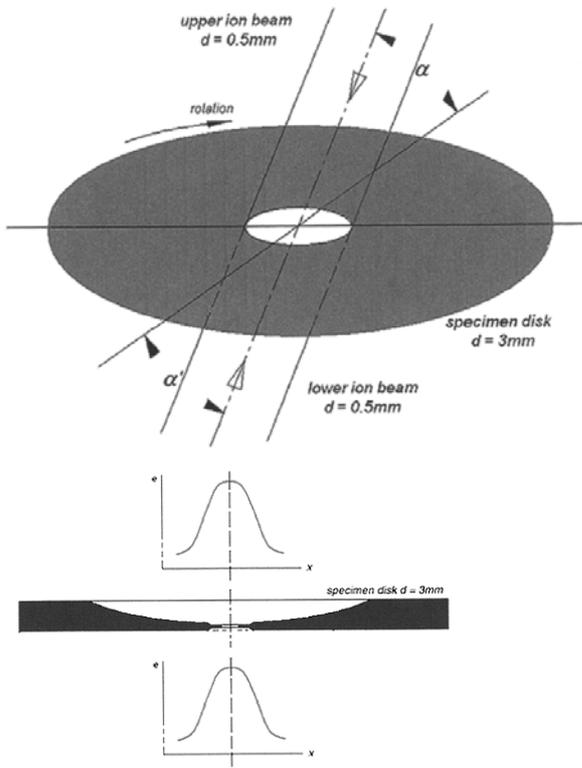
The figures show the results of ion-milling preparation of an aluminium oxide ceramics. On the left side the conventional ion-milling procedure is exhibited and on the right side results obtained with the “non-centric” method. The TEM-image of the centric milled specimen shows a central hole only with a small electron transparent specimen area. The right image of the same ceramics shows a considerably larger electron transparent specimen region with many small holes over the thinned surface thus opening the way for a better examination of the specimen in the TEM.

Tests with different materials have shown, that non-centric ion-milling in most cases results in specimens with larger electron transparent regions. Two subjects of interest should be pointed out when applying this method: Firstly, it is very important to adjust the two ion-beams not too far from the center of the specimen disk. For the exact alignment of the beam at the upper and the lower side, we use a glass disk as fluorescent light shield with 3 mm diameter and 0.1mm thickness (made from cover slips with an ultrasonic disc cutter). Beams which are placed too wide from the center of the specimen disk may cause deposition of sputtered material on the specimen from other parts of the specimen holder. Secondly, the thinning time of the ion-beams because of the non-centric adjustment is much longer (estimated factor two) than by centric thinning.

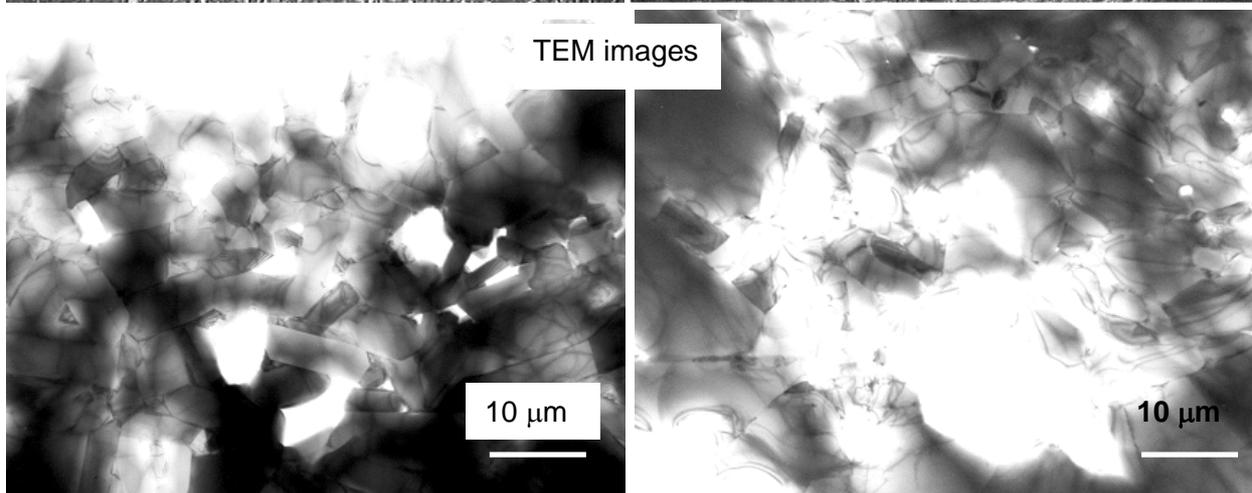
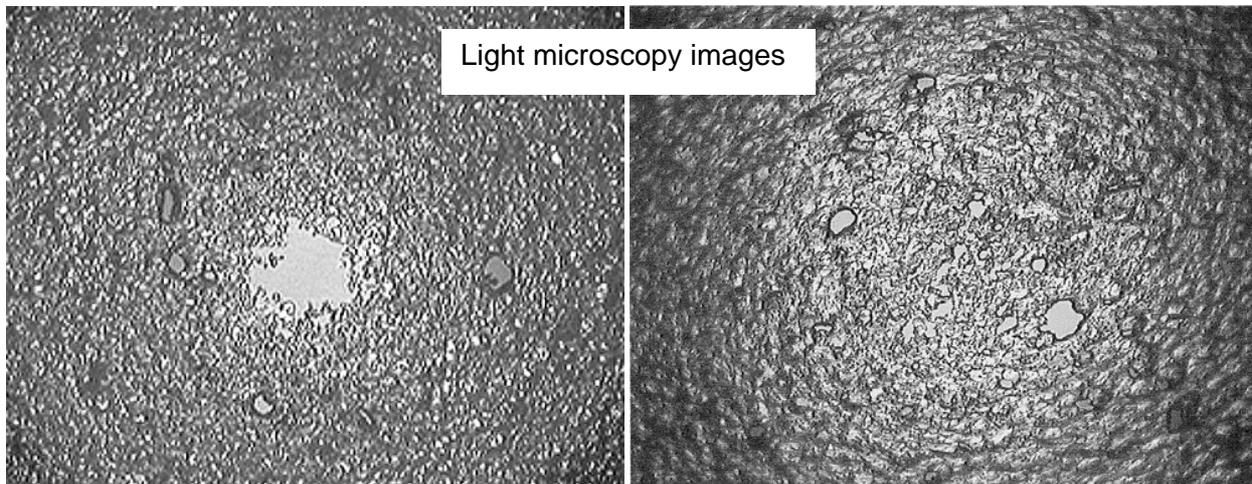
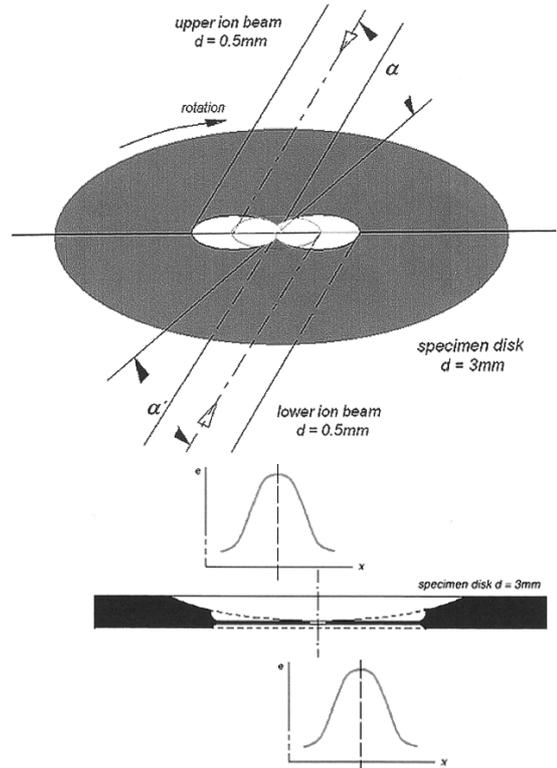
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