JEELS 2024
13d edition
2 July - 4 July 2024
Toulouse
Many thanks to our sponsors
Dear colleagues,

We are delighted to welcome you to the 13th edition of the “Journées de l’EELS”: JEELS 2024 congress, which takes place in Toulouse in the CEMES laboratory, from 2nd to 4th of July 2024. In the continuity of the last JEELS edition that took place in Munster with the German EELS community, this edition will be a join congress between french and spanish communities.

Recent substantial advances in electron optics, gun brightness, electron monochromators, new spectroscopic instrumentation and detectors have motivated the development of multiple fast-electron-based spectroscopies capable of atomic-scale spatial resolution and the use of complementary EM-based techniques for material science. JEELS 2024 will be a forum for discussing the current status, new developments and the perspectives for techniques, instrumentation, and data analysis.

The conference scope includes:

- Correlative Spectroscopies for materials science
- Advanced instrumentation, signal and image processing
- Low-energy excitations
- Theory applied to electron spectroscopies
- Operando
- New Spectroscopies

Contributions highlighting the complementarity of novel EM-based techniques with non-based electron techniques will be presented, as well as contributions in materials chemistry, condensed matter, physics soft matter and biomaterials. Sponsoring industrial partners will present their latest developments within the session most appropriate to their subject.

Organizing Committee:

Pier-Francesco Fazzini, CEMES, Toulouse
Teresa Hungria, Centre Castaing, Toulouse
Sophie Meuret, CEMES, Toulouse
Cécile Marcelot, CEMES, Toulouse
Bénédicte Warot-Fonrose, CEMES, Toulouse

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Cécile Hébert, EPFL, Lausanne
Pascale Bayle-Guillemaud, CEA-Minatec, Grenoble
General information

Phone numbers

If you have questions during the conference, please call +33 6 67 11 60 31 (Bénédicte Warot-Fonrose) or +33 6 52 72 33 58 (Teresa Hungria)

Access to the CEMES lab

CEMES is located on the banks of the Canal du Midi, in the Rangueil district in the south-east of Toulouse. It is a 4-minute walk from the Saouzelong metro station (line B) and the Saouzelong bus station (line 44). The “Tisséo” web site or app can give you itineraries.

CEMES-CNRS
29 rue Jeanne Marvig, BP 94347
31055 Toulouse Cedex 4, France
Link to Google Maps.

Access to the Castaing center

We will move to the Castaing center at the coffee break (Tuesday only) to attend the poster session and visit the center. A dinner will be served in the hall of the center. We will indicate how to get to the center, either by bus (Clement Ader bus station), bike or car.

“L’espace Clément Ader” hosts the Castaing center, all directions are indicated here. Location : 3 Rue Caroline Aigle, 31400 Toulouse
Poster session

Poster size is A0 (841 mm x 1189 mm).
The first poster session will be organized in the Centre Castaing on Tuesday afternoon, after the coffee break.
Posters will be presented in the CEMES Hall from Wednesday morning till Thursday noon.
We will take care of the poster transfer on Tuesday night.

Catering

We will share coffee breaks on Tuesday afternoon, Wednesday morning and afternoon and Thursday morning.
A dinner will be served at the Castaing centre on Tuesday night.
A buffet will be served for Wednesday lunch and we will meet in the "Moai "restaurant for the gala dinner on wednesday night. The restaurant is close to the “jardin des plantes" in Toulouse city center (location : 35 All. Jules Guesde, 31000 Toulouse).

Wifi access

An eduroam wifi access is available in the CEMES lab and in the Castaing center.
# Program

**Tuesday 2d July**

## Session 1: Electron spectroscopies

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## Posters

**P1** - Electronic properties of 2D Transition Metal Dichalcogenides ternary alloys: an ab initio study, *N.F. Andriambelaza*

**P2** - In situ electron beam irradiation of Ti3C2Tz MXenes. A STEM-EELS study, *A. Benmoumem*

**P3** - Eu3+-doped Y2O3@SiO2 core@shell structures: a comprehensive study on the formation of Y2SiO5 hollow spheres, *F. Borges*

**P4** - Structural and chemical study of interfaces in TiAlN/TiAl multilayers, *C. Bouillet*

**P5** - EELS Spectra classification: Machine Learning vs Neural Network, *N. Brun*

**P6** - EELS contribution to the study of VO2 electrochromic films, *S. Buffiere*

**P7** - Free electron spectroscopy seen through the prism of quantum optics, *T. Fraysse*
P8 - CLE for studying quasi-particle excitations and the quest of suppressing transition radiation, A. Freilinger

P9 - AI Automation for Transmission Electron Microscope Alignment, L. Grossetête

P10 - Cationic ordering in natural spinel structures, M. Marinova

P11 - Correlating the chemical structure and plasmonic properties of bimetallic nanoalloys, M. Moreira

P12 - Electron microscopy: an efficient tool to evaluate UCNPs complex structures for bioimaging applications, L. Passini

P13 - Microcharacterization of medieval fire-gilded Cu jewellery by EDS and SAED analysis, A. Pugliara

P14 - Towards electron beam shaping in an Ultrafast Transmission Electron Microscope, V. Rollo

P15 - TEM/STEM investigations of an unexpected contrast asymmetry in topological insulator BiSb and in pure Bi, L. Rubiola

P16 - Study of nanolaser optical and structural properties at the nanometer scale, C. Santini

P17 - Structural, chemical and magnetic correlations of chromite epitaxial thin films, B. Warot-Fonrose

P18 - Studying the titanium oxidation in reactive thin films via electron microscopy, T. Wu
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#### Session 7: New spectroscopies (time resolved, vortex beams…)

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Oral contributions
Advances in data analysis strategies for EELS


¹ LENS-MIND, Department of Electronics and Biomedical Engineering, Universitat de Barcelona
² Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona
³ Electron Spectrometry and Microscopy Laboratory, École Polytechnique Fédérale de Lausanne

In recent times, there have been substantial improvements in both the spatial and energy resolution of Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS) because of several technological advancements, such as aberration correction, monochromators, direct detectors, and increased computational power. EELS has thus evolved from acquiring a single spectrum in several seconds with a spatial resolution of tens of nanometers to atomic resolution spectrum images (SI) with thousands of pixels acquired in milliseconds, which raises the question of which is the best way to deal with such amount of data.

In the EELS community there is a widespread use of dimensionality reduction algorithms, typically for denoising, combined with traditional Egerton quantification or some sort of model fitting, especially if the quantification problem is ill-poised [1].

Yet, analyzing EELS SIs to map the spatial distribution of properties reflected in the shape of individual EEL spectra can be thought of as classifying spectra into groups with similar characteristics, which is what clustering algorithms do. One of the most popular ones is agglomerative clustering, which has been proved useful for EELS [2]. More advanced clustering strategies, such as the combination of Hierarchical density-based spatial clustering of applications with noise and uniform manifold approximation and projection yield an improved performance [3]. The combination of clustering analysis for segmentation and non-linear least squares fitting for spectral analysis has been proposed as a robust EELS quantification strategy with a low computational cost, made available through the open access software WhatEELS [4].

Machine Learning supervised approaches involve training ML models using labeled data, where the desired output or target is known. These models learn from the labeled examples to make predictions or classify new, unseen data. Supervised strategies based on Artificial Neural Networks (ANN) [5,6] and, especially, on Support Vector Machines (SVM) [6,7] and have been successfully applied to EELS and proven to classify EEL spectra with very high accuracy and low computational cost, if a training set is available. These strategies are currently being incorporated into WhatEELS for transition metal oxides.

References

Title: Innovative internal coatings for pharmaceutical bottles

C. Genevois¹, B. Diallo¹ K.C. Topka²,³, B Caussat², C. Vahlas³ and N. Pellerin¹.

1. Conditions Extrêmes et Matériaux : Haute Température et Irradiation (CEMHTI), Université d’Orléans, UPR3079 CNRS, Orléans, Cedex 2, France
2. Laboratoire de Génie Chimique (LGC), Université de Toulouse, CNRS, Toulouse, France
3. Centre Interuniversitaire de Recherche et d’Ingénierie des Matériaux (CIRIMAT), Université de Toulouse, CNRS, Toulouse, France

The pharmaceutical industry faces the limits of sustainable packaging of certain medications because interactions can occur between the glass bottle and the liquid medication. The surface of the glass deteriorates and fragments of glass can pass into the medicine. Hence the idea of depositing an inert protective film on the internal surface of the bottle. During the project (ANR Healthyglass) the chemical deposition process from a vapor phase made it possible, initially, to deposit different films on a flat silicon substrate (wafer) by varying the chemical precursors as well as the deposition conditions in the reactor [1-4]. The microstructure and the chemistry of these different coatings have been characterized by several techniques including the electron energy loss spectroscopy (EELS). Indeed, the nano-scale organization is the basis of the mechanical and chemical resistance of the coating as well as its ability to adhere to the substrate. The coatings are composed of light elements (Si-O-C-N) which are well detected by EELS. The processing of the spectrum-imaging by the MLLS fitting approach on the Si K-edge made it possible to highlight the existence of different layers at the substrate/film interface. Moreover, the combined approach of EELS elemental mapping and PCA (Pluri-component Analyses) processing highlighted nano-enrichment in certain films.

References:

Figure 1. Amorphous film deposited on a Si-substrate (left) and EELS elemental cartographies showing nano-enrichment in N and Si (right).
Thermal Crystallization of Amorphous Ge-rich GeSbTe Layers Deposited on a Polycrystalline GeSbTe Template: the effect of N doping

Minh-Anh Luong and Alain Claverie

CEMES-CNRS and Université de Toulouse, 29 Rue Jeanne Marvig, 31055 Toulouse, France

We report detailed experimental studies of the thermal crystallization of amorphous off-stoichiometry Ge-rich GeSbTe layers (a-GGST) deposited on a polycrystalline Ge$_2$Sb$_2$Te$_5$ substrate (c-GST). We show that the undoped a-GGST layers crystallize by solid-phase epitaxy (SPE) on the c-GST template while, when N doped, they crystallize by homogenous nucleation within the a-GGST layer. By combining in-situ annealing in the transmission electron microscope and ex-situ chemical analyses using electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX), we unveil the mechanisms at the origin of this change of behaviour resulting from doping. In the undoped layers, STEM EELS maps show that the Ge atoms in excess to the regular stoichiometry of Ge$_2$Sb$_2$Te$_5$ are continuously transferred during annealing from the a-GGST layer into the polycrystalline substrate where they can diffuse rapidly and segregate at grain boundaries (Figure 1). This fast transfer results in a local depletion of “mobile” Ge atoms in front of the interface. Consequently, the amorphous material is locally of the same stoichiometry than the crystalline template, which allows its crystallization by SPE. When the a-GGST material is N doped, the excess Ge is still transferred into and segregates within the c-GST layer but the high viscosity of the amorphous material resulting from its doping with N (i.e. the lower diffusivity of Ge in this layer) does not permit the build-up of such a Ge depleted region in front on the crystalline template. Instead, crystallization occurs homogenously within the amorphous layer, and but needs a much higher temperature to be activated. Details of the interchange of atomic species at the interface during these processes have been revealed by EDX (Figure 2) and REF 1.

References:

Figure 1. HAADF images and RGB EELS mapping of the c-GST / a-GGST structure, annealed at 300°C for different time durations. Ge, Sb and Te are displayed in red, green and blue colors, respectively.

Figure 2. EDX line profiles showing the evolution of the chemical distributions of Ge (red), Sb (orange) and Te (cyan) during ex-situ isothermal annealing at 310 °C. (a), as-deposited sample, (b), after 30 min, (c), 4 h, (d), 16 h and (e), 24 h annealing. (f) is a Dark Field image and associated diffraction pattern of the sample annealed at 310 °C for 84 h showing that all these atomic interchanges occur while the N doped GGST layer is still amorphous.
Expanding the boundaries of EELS through advanced integration of the new EELS filter

Maria Meledina\textsuperscript{1}, Bas Cornelissen\textsuperscript{1}, Terry Dennemans\textsuperscript{1}, Sander Henstra\textsuperscript{1}, Dileep Krishnan\textsuperscript{1}, Sorin Lazar\textsuperscript{1}, Sjaak Thomassen\textsuperscript{1}, Peter Tiemeijer\textsuperscript{1}, Wouter Verhoeven\textsuperscript{1} and Paolo Longo\textsuperscript{1}.

\textsuperscript{1} Thermo Fisher Scientific, Eindhoven, the Netherlands

Electron energy loss spectroscopy is a well established technique applied to the advanced materials to investigate their structure, chemistry and electronic properties at the local scale. For EELS investigations the setting of both the TEM and the EELS filter optics plays a crucial role for the reliable high quality of the produced data. The optics of the whole EELS setup is rather challenging: a broad range of electron energies must be simultaneously transferred through the microscope and through the spectrometer, from specimen to detector, without introducing chromatic blur or chromatic distortions. Together with it, when optimising the experimental conditions aiming for the specific results one is constantly modifying the setting of both the microscope, such as the camera length, and the spectrometer, for example, the dispersions – introducing the extra challenges to maintain the accurate transfer.

To ensure the superior performance and the quality of the EELS data, we closely integrated the optics of the TEM and the EELS filter. Together with this, the close integration of the EELS filer and the TEM column expands the possibilities for the multimodal use of the advanced TEM techniques, such as for example simultaneous EELS and EDX.

In this contribution we will talk on the advances of close integration of the TEM column and the EELS filter and highlight it with several practical examples.

\textbf{Figure 1.} MultiEELS for DyScO\textsubscript{3}: Top: without correction. Bottom: with dynamic auto-correction.
Photon-Correlation Cathodoluminescence Spectroscopy in a SEM

Gwénolé Jacopin*

1 Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France
*Corresponding author: gwenole.jacopin@cnrs.fr

To establish the relationship between luminous efficiency and material characteristics, precise measurement of radiative and non-radiative recombinations is essential. While time-resolved photoluminescence spectroscopy is commonly used for this, it falls short in offering nanoscale resolution necessary for defect characterization.

To go beyond these limitations, fast electrons can be used as a highly localized excitation source for luminescence measurements. This technique is called cathodoluminescence (CL) spectroscopy. Recently, picosecond time-resolved CL technique has been developed to reach the same time high spatial and high temporal resolutions [1]. However, building a high-brightness pulsed electron gun remains a challenge, causing reduced spatial resolution, low CL intensity, or photocathode aging problems.

In this work, to circumvent these limitations, inspired by the pioneering work of Meuret et al. [2], we took advantage of the specific statistics of electron-hole (e-h) pair generation by fast electrons. Indeed, in a secondary electron microscope, the interaction of the incident electron with the semiconductor generates almost instantaneously (< 1 ps) a bunch of e-h pairs (typically > 300). These e-h pairs can then radiatively recombine with a probability that decreases with time, according to their carrier lifetime. Hence, by studying the autocorrelation function of the CL intensity ($g_2(\tau)$), a strong bunching is expected ($g_2(\tau = 0)>> 1$). More importantly, by fitting $g_2(\tau)$, we access to the local carrier lifetime without the need for a pulsed electron gun [3]. Thus, to measure the carrier lifetime at the nanoscale, we built a Hanbury Brown and Twiss interferometer to analyze the CL photon statistics [4]. We apply this method to investigate different optoelectronic devices ranging from blue µ-LEDs to deep-UV nanowire based LEDs.

References:

Figure 1. Schematic diagram of the experimental setup
Fast Automated Phases Separation in Industrial Stainless Steel by Combining Low-Loss EELS Experiments with Machine Learning-based Algorithms

Beatriz Amaya Dolores¹, Victoria Castro Riglos¹, Ashwin Ramasubramaniam², Lorena González-Souto¹, Rafael Sanchez³, Javier Botana¹, Juan F. Almagro³, José J. Calvino¹ and Luc Lajaunie¹

¹ Departament of Materials Science and Metallurgical Engineering and Inorganic Chemistry, Faculty of Sciences, Universidad de Cádiz, Campus Río San Pedro S/N, Puerto Real, 11510 Cádiz, Spain
² Department of Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, USA
³ ACERINOX EUROPA SAU, Technical Department, Pol. Industrial Palmones S/N

Introduction. Duplex stainless steels (DSS) undergo phase transformations during aging as the precipitation of the Cr-Mo-rich σ phase at the α/γ interface, damaging its mechanical and corrosion properties [1]. Low-loss EELS provides a quick acquisition of large datasets due to its high signal intensity. However, interpreting the data is complex due to excitation processes like volume plasmon [2]. In this study, a novel method using low-loss EELS is developed to automatically identify phases in both as-cast and aged industrial DSS. This method enables mapping of α and γ phases as well as intermetallic phases such as the σ phase.

Experimental. As-cast and aged DSS were fabricated at the ACERINOX EUROPA SAU plant. TEM samples were studied by using a FEI Titan Cubed Themis 60-300 microscope operating at 200 kV. EELS datasets were clustered by using the “kmeans++” algorithm. The only parameter needed was the number of clusters determined by using the silhouette metric [3]. To compare with more classical approaches, EELS dataset were also fitted pixel per pixel by using the Drude model in order to map the plasmon energy and plasmon width parameters.

Results. Figure 1a and 1b shows the annular dark field image and EELS spectra acquired on an as-cast DSS along an α/γ interface boundary. The plasmon of both phases are well separated by about 2 eV. Figure 1c and 1d shows the results of the k-means clustering. The clustering reproduces really well the α and γ domains and there is a nearly perfect match between the cluster centers and the representative EELS spectra. Figure 2a shows the superposition of Cr elemental map and dark field image along an α/γ interface boundary of an aged sample. Precipitates rich in Cr belonging to the σ phase can be observed along the interface. The silhouette metric indicates that three clusters for this dataset are needed in this case. Figure 2c and 2d shows the cluster centers and clusters maps, respectively. All these results show that automatic phase separation in DSS can be successfully performed by combining low-loss EELS experiments and k-means clustering.

References
**Figure 1.** As-cast sample a) ADF image acquired simultaneously as the EELS dataset b) EELS spectra acquired on the α and γ phases. c) Results of k-means clustering and d) corresponding cluster centers.

**Figure 2.** Aged sample a) Superposition of Cr elemental map and DF image. b) Estimation of the number of clusters c) Results of k-means clustering and d) corresponding cluster centers.
Nanoscale Vibrational Spectroscopy of Space Weathering from Asteroid Ryugu

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Airless bodies are subjected to space-weathering effects that modify the first few microns of their surface. Understanding their impact on the optical properties of asteroids is key to the interpretation of their color variability and infrared reflectance. The Hayabusa2 sample return mission to asteroid Ryugu offers the first opportunity to study these effects in the case of the abundant C-type asteroid belt objects. We use vibrational EELS at high spatial resolution to measure the distinct mid-infrared spectral signature of the space-weathered surface, revealing the loss of structural -OH and C-rich components in the space-weathered layers, compared to the underlying matrix. Exposure to the space environment thus tends to mask the optical signatures of phyllosilicates and carbonaceous matter. Our findings should contribute to rectifying potential underestimations of water and carbon content of C-type asteroids when studied through remote sensing with new-generation telescopes.


Figure 1. Vibrational-EELS of Ryugu space-weathered and unweathered samples compared with $\mu$-FTIR data and phyllosilicate reference samples
Electronic excitations in thin layer materials: insight from classical electromagnetism to ab initio calculations

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Time Dependent Density Functional Theory is an ab initio longitudinal formalism which allows the calculation of the macroscopic average of the inverse dielectric function. This quantity leads to the electron energy loss spectrum (EELS). For 3D crystals, such a quantity can be related to the absorption spectrum, which is a transverse response. This is based on i) the Adler and Wiser formula [1], which relates the macroscopic average of the dielectric function to the macroscopic average of the inverse dielectric function and ii) the Ehrenreich demonstration for the equivalence of the transverse and longitudinal contractions of the dielectric tensor [2] in the optical limit. Following our investigations on electronic excitations on quasi-2D objects [3], we have evidenced that the 3D formalism fails. It results that the loss spectrum and the optical response are similar and reveal to be a linear combination of the absorption and the plasmon bulk spectra. This quantity presents the same features as the transmittance or the reflectance of an electromagnetic field impinging an ultrathin layer [4, 5]. These results have been demonstrated on a thin layer of silicon since the absorption and plasmon resonance can be easily distinguished, but the conclusions apply to the more natural 2D materials like a stacking of few layers of graphene, and should be measured in EELS.

References:


Figure 1. Comparison of loss spectrum (left) and the optical response (right) for a thin slab of silicon.
Meet the Mönch: light collection and injection in a Transmission electron microscope
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First developed by Kociak and Zagonel[1], the Mönch is a new add on for transmission electron microscopes, capable of performing advanced cathodoluminescence experiments, as well as injecting in a tightly focused spot directly on a TEM sample. This contribution will discuss the recent advances made at Atolight to better characterize and expand the Mönch capabilities. Particular focus will be given to the mirror design and detection line. In particular, the influence of mirror thickness on detection performance will be discussed, since this is a key parameter that needs to be adapted to a TEM pole piece gap.

References


Figure 1 Ratio of photons reflected by the mirror as a function of its thickness for 3 extreme examples of emitters. Absorption by the mirror and coupling efficiency of the light into the detection system are not taken into account.
Addressing the challenges of low signal-to-noise in TEM: optimizing signal collection and analysis

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Transmission electron microscopy (TEM) stands as a potent instrument in materials science, offering insights into structure, chemical composition, and physical properties ranging from the micrometer to the angstrom scale. However, harnessing this tool presents challenges for microscopists, demanding mastery of material-specific nuances, intricate microscope alignments, and post-acquisition data processing. On top of that, experimentalists often contend with weak signals, whether due to the material's sensitivity to the electron beam or the indirect nature of the observed interaction processes. Low signal-to-noise ratio brings several issues: it becomes hard to align the microscope correctly, and the data analysis becomes significantly more complex.

In this contribution, we will explore methods to enhance signal collection by utilizing dedicated hardware, assist in decision-making during experiments using deep learning algorithms, and improve data analysis by integrating physics modeling into machine learning algorithms.

In the first part of this presentation, we will discuss the properties of direct electron detection (DED) devices and how they can enhance signal collection. We will illustrate how DED can be used for the study of astro-materials with a preliminary investigation of beam-induced damages on beam-sensitive polymers.

Next, we will demonstrate how physics modeling can be used to craft efficient deep learning and unsupervised learning algorithms. Firstly, we will show how to build a linear model of scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDXS) and incorporate that model into a non-negative matrix factorization (NMF) framework. This physics-based machine learning method helps reduce the artifacts of NMF. It also leverages prior knowledge about the sample to improve data analysis.

Finally, we will illustrate how deep learning can be a useful tool for real-time decision-making. This will be exemplified through the simulation of photon-induced near-field electron microscopy (PINEM) and the real-time determination of its underlying physical parameters. We will demonstrate that both deep learning and unsupervised learning methods yield accurate results even with a very low signal-to-noise ratio.
Absolute Correction of HR-(S)TEM and Low Magnification TEM Images from Distortions and Calibration Errors

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TEM and STEM imaging are widely used techniques for visualising and quantifying shape, size, density, composition, strain and structure in solid state materials at micro-, nano- and subnanometer scales. Such images are subjected to different types of distortions and calibration errors. For the purpose of fully quantitative analysis, these distortions should be removed. We propose here several methods for the correction of low magnification TEM, high-resolution TEM (HR-TEM) and STEM (HR-STEM) images.

For the correction of low magnification images taken at a basic conventional TEM we apply the technique named “Moiré by specimen design” (MoSD) [1] which allows to measure deformation in single-crystal structures, in cross-sectional and plan view geometries, with nanometric resolution over a micrometre field of view. The method is based on a specific sample preparation of a stack of two superimposed rotated lamellas of known single crystal that provides the formation of “controlled” moiré images. The deviation of experimentally obtained pattern from the anticipated one can be quantitatively mapped by reciprocal space treatment. We developed a method which allows to correct any other image for these distortions that will be illustrated by different examples.

For HR-(S)TEM images, we present a method named “Absolute strain” (AbStrain) [2]. It allows for quantification and mapping of interplanar distances and angles, displacement fields and strain tensor components with reference to a user-defined Bravais lattice and with their corrections from the image distortions. AbStrain goes beyond the restriction of the existing method known as geometric phase analysis by enabling direct analysis of the area of interest without the need for reference lattice fringes of a similar crystal structure in the same field of view. For the case of a crystal composed of two or more types of atoms, we also present a method named “Relative displacement” [2] for measuring relative atom displacements of the sub-structures in the unit cell. The successful application of AbStrain and Relative displacement to HR-STEM images of functional oxide ferroelectric and semiconductor heterostructures will be demonstrated.

References:

Highly Efficient Machine Learning Strategies for the Characterization of Low-Loss Electron Energy Loss Spectroscopy: Nanophotonic Resonances as a Case Study

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Localised Surface Plasmon Resonance (LSPR) is a non-propagating electron-density wave that is confined at the surface of a metallic nanoparticle. They can enhance the electromagnetic radiation, concentrating it into sub-wavelength volumes. Its resonance can be tuned by changing the surrounding medium and its geometry. This unique property opens a wide range of applications across various fields of applied research such as nanophotonics, robotics, environmental studies, energy, biology, and medicine.

Electron Energy Loss Spectroscopy (EELS) within a Scanning Transmission Electron Microscope (STEM) has revealed remarkable capabilities in the analysis of plasmons at nanometric scale, as this technique achieves sub-angstrom spatial resolution and can excite the complete range of LSPR modes supported by the nanostructure. By employing EELS, the plasmonic properties can be correlated with geometric or structural characteristics, enabling a more comprehensive understanding of the plasmonic response.

In this study, based on the analysis of Silicon/Gold nanopillars samples, we demonstrate that clustering techniques can be used for detecting LSPRs in EELS. We propose a novel combination of unsupervised machine learning strategies that detect LSPRs in EELS spectrum images. To demonstrate the effectivity of this methodology, we studied Si/Au nanopillars. The detection of LSPRs is done by reducing the dimensionality of the data, clustering this low-dimensional space, and recuperate the spatial space. We demonstrate that using this methodology, it is possible to recover the LSPRs, among distinct spectra in a large EELS dataset, and easily make a plasmonic spatial map without the need for prior knowledge or labelling of the data.

References:

Innovative data augmentation for supervised classification in Electron Energy Loss Spectroscopy using Generative Adversarial Networks

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Recent advancements in Scanning Transmission Electron Microscopy (STEM), particularly with Electron Energy Loss Spectroscopy (EELS), have been driven by technical improvements in the equipment such as aberration correctors, direct detectors, and enhanced computing power. These developments have led to the acquisition of large datasets, underscoring the need for efficient data management and analysis tools within the STEM community. Machine Learning (ML), categorized into supervised (requiring previously known/labeled data) and unsupervised (independent of prior data) learning, has become a powerful tool in EELS for tasks like classification [1-3], clustering of spectrum images [4-5] or denoising [6]. However, while unsupervised learning may appear preferable due to this lesser requirement on prior data, it requires great caution due to the complexity of interpretation of EELS data, and the output of these algorithms may not always provide physical insights on the materials’ properties of interest.

This study therefore addresses a significant challenge in applying supervised algorithms instead to classify EELS: the requirement for substantial amounts of labeled data, which may be difficult to acquire because sample susceptibility to electron beam damage. To mitigate this, we introduce a novel approach employing data augmentation with Generative Adversarial Networks (GANs) [7] for EEL spectra generation. This strategy effectively generates synthetic spectra from a small set of experimental data. By including spectra from different instruments and samples, we significantly increase the diversity of the generated data, reducing dependence on large experimental spectra datasets for training these GANs, whereas maintaining data robustness and variability.

In the context of supervised learning, this method becomes an effective data augmentation strategy, because the comprehensive generated data can be used as suitable training datasets for generalized classifiers, mitigating the need to acquire large volumes of experimental spectra.

References:
[8] This work was supported by the Spanish Project PDC2021-121366, PID2019-106165GB-C21 and PID2022-138543NB-C21, the ELECMI-ICTS, the AGAUR 2020 FI-SDUR grant, and by the Engineering and Physical Sciences Research Council (EP/W021080/1).
CEFID: A flexible platform for advanced spectroscopic experiments

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The CEOS Energy Filtering and Imaging Device (CEFID) is an energy filter and spectrometer offering state-of-the-art specifications and the flexibility to implement ambitious and unprecedented experiments. The filter design comprises highly optimised and stable optics up to the energy-selecting slit, and a flexible and minimalist projective stage [1]. This gives high performance and stability, while allowing to hop between modes (imaging, spectroscopic dispersions) with little to no re-tuning. The Python/Qt-based graphical software used for the filter operation, implements interactive and automated procedures for alignments, common workflows ranging from EFTEM to 4D-STEM, and tools for on-the-fly analysis from live DFT to EELS maps computation. A wide range of detectors (Fig. 1) and scan generators from different manufacturers has already been integrated and can be used for both the tuning and data acquisition. The software is highly extendable and offers a scripting and plug-in API in Python and a remote control interface for the integration into third-party software. The capability and versatility of the system make it well suited for rapidly acquiring and evaluating spectroscopic information on samples of interest [2], while its flexibility and compatibility make it a platform for complex experiments where different tools need to work in unison, such as the synchronization of acquisition with in-situ stimuli, or photon-induced near-field electron microscopy with dedicated detectors and low count rates [3].

References:
[3] We would like to thank all our partners and customers who accompany us on this journey.

**Figure 1.** Rendering of CEFID outfitted with cameras from TVIPS, Amsterdam Scientific, Direct Electron, Dectris and Quantum Detectors and a retractable ADF detector developed by CEOS together with PNDetector. Each detector has its specific strengths which make it ideal for a class of experiments. Typically, one to three detectors are installed at a time.
Interplay between structure, chemistry and magnetism in 3D ferromagnetic nanostructures grown by FEBID

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In the last decade, novel nanofabrication methods and high-resolution characterization techniques have paved the way to study the nanomagnetism in three-dimensional (3D) objects, which has become a central topic in the field of Magnetism. 3D ferromagnets have been proposed as building blocks for future spintronic devices such as high-density magnetic memories, nano-sensors or logic devices [1] based on the exotic magnetic properties of the novel spin textures induced by 3D geometry. In this context, Focused Electron Beam Induced Deposition (FEBID) plays a crucial role as a direct-writing, one-step nanolithography technique, which has become ideal for prototyping novel 3D ferromagnetic nanoarchitectures [2]. In this Lecture I will review the work performed during the last years in the development of 3D ferromagnetic nanostructures of cobalt and iron grown by FEBID, including ferromagnetic nanowires (NWs), core-shell NWs, and magnetic nanotubes (NTs). We will demonstrate that the magnetic properties of 3D magnetic nanostructures are determined by the correlation between the structure, geometry and chemistry as a function of the growth conditions [3]. Thus, the optimization of the growth conditions to achieve optimal functional properties was only been achieved by correlative realization of different electron microscopy techniques, including HRTEM, STEM, EELS, EDX and off-axis electron holography on the same objects, as illustrated in Figure 1.

References:

Figure 1. Correlation between microstructure (HRTEM), chemical composition (EELS) and magnetism (electron holography) in Co-FEBID 3D nanowires upon high-vacuum thermal annealing [3].
Internal pressure in Xe bubble induced by ion irradiations in UO$_2$: TEM/EELS studies
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During the fission reaction, ceramic-type UO$_2$ nuclear fuel undergoes structural modifications and significant chemicophysical changes. The fission reaction generates two fission products and about 15% of these are gaseous, with a majority of xenon atoms [1]. Since Xe atoms are insoluble in UO$_2$, they can precipitate into bubbles. The latter can reach subnanometric up to micrometric sizes and being highly pressurized [2]. In addition, experimental characterization revealed faceted bubbles in specific irradiation conditions [3]. These bubbles have an impact on the fuel microstructure and property changes (swelling, cracking...). The nuclear industry's high requirements involve a better appreciation of irradiated fuel behavior. In the context of upstream research, a better understanding of the nucleation and growth mechanisms of these fission gas bubbles, and of the influence of their pressure on these mechanisms is required. It is with this objective that a separate effect study was implemented. Using Xe ion implantations followed by different annealing conditions enabled us to obtain various bubbles populations and pressures. Electron energy loss spectrometer (EELS) is used to obtain the quantity of Xe atoms present in the various bubbles, then the diameter of the bubbles is obtained using transmission electron microscopy methods in parallel beam mode (TEM) or in scanning mode coupled with a high-angle annular dark-field detector (STEM-HAADF). This enables us to estimate the volume of the bubble using the spherical hypothesis. At last, knowing the number of gas atoms present in the bubble and its volume, the internal pressure of the bubble can be determined thanks to an appropriate equation of state of Xe [4]. After the validation of the method on the implanted fuel, the study will be performed on the fuel irradiated in reactor.

References:


Figure 1.
STEM-HAADF image: UO$_2$ implanted with 390 keV Xe, annealed at 1500 °C/1 h.

Figure 2.
EELS image: mapping of Xe in the implanted UO$_2$ (680-730 eV).
Advanced EELS spectroscopy characterization of AlGaN/GaN-based HEMT devices

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The combination of STEM (Scanning Transmission Electron Microscopy) with electron energy-loss spectroscopy (EELS) and Electron-Loss Near-Edge Structure (ELNES) has gained great interest in the microelectronics industry. Indeed, ELNES can provide additional information on local atomic and electronic structures of materials compared to the already commonly used XEDS (X-ray Energy Dispersive Spectroscopy) method for chemical quantification. This project intends to investigate High-Electron Mobility Transistor (HEMT) devices based on AlₓGa₁₋ₓN semiconductors for high-power and high-frequency applications [1], using EELS. TEM experiments are performed on a probe Cs-corrected JEOL Neo-ARM 200F equipped with a Cold-FEG and a GIF (Gatan Image Filter) Continuum spectrometer.

The HEMT device presented in this work is composed of a GaN channel and an AlGaN barrier structure separated by a few-nanometer AlN spacer grown to improve the performance of the 2-Dimensional Electron Gas (2DEG) formed at the interface [2]. Due to significant lattice mismatch between GaN and Si, an AlN nucleation layer is grown first on 300 mm Si wafers. Successive AlₓGa₁₋ₓN buffer layers with decreasing amounts of Al are then needed to accommodate stress in the structure. This buffer stack allows the growth of an ideally crack-free GaN channel as shown in Fig. 1, assuring optimal electron mobility in the device. Preliminary work has already been conducted to observe the variation of the N K edge ELNES structure along the buffer layer stack at 200 kV, highlighting the transition between layers [Fig. 2 (a)]. Likewise, the observation of the plasmon peak in the valence region along the buffer stack has demonstrated a linear dependency between the plasmon energy peak (Eₚ), and the composition of Al; xAl [Fig. 2 (b)]. Additional work has been carried out to improve TEM sample preparation and further experiments will be performed to investigate the contribution of lower acceleration voltage (i.e. 80 and 60 kV) on the N K edge, especially around the 2DEG channel/barrier interfacial region.

References:
[3] The authors thank the French Association Nationale Recherche Technologie (ANRT) for fundings provided as a part of the CIFRE n°2022/1324 agreement between STMicroelectronics (Crolles2) SAS and ANRT.

Figure 1. (a) TEM micrograph of HEMT device, (b) STEM-HAADF image of the AlₓGa₁₋ₓN buffer layer stack

Figure 2. (a) ELNES spectrum of N K edge and (b) plasmon peak analysis along AlₓGa₁₋ₓN buffer layer stack
Unraveling the Oxidation Dynamics in Zr/CuO Nanothermites Using Correlative Spectroscopies
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Refractory metal fuels like zirconium (Zr) possess the capability to undergo rapid oxidation and exhibit exceptional combustion efficiency, making them highly reactive when combined with a strong oxidizer such as CuO. The rapid reaction rates, however, have hindered a comprehensive understanding of the reaction mechanisms from a fundamental perspective.

In this study, Zr/CuO reactive multilayer films (RMF) are deposited via a carefully controlled physical vapor deposition (PVD) process, ensuring precise regulation of film thicknesses. The fabricated CuO/Zr stacks are annealed at temperatures (Figure 1) corresponding to key oxidation events, followed by a detailed analysis of each interface. This study then delves into the evolution of oxidation states of zirconium (Zr) in Zr/CuO nanothermites, shedding light on their reaction mechanisms.

Figure 1. STEM micrographs of CuO-Zr-CuO-Al reactive multilayer films at various temperatures. Al is used as a capping layer.

Utilizing correlative spectroscopies, including electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX), we also examine the Zr layer within reactive multilayer stacks. EELS proves instrumental in analyzing both high-loss and low-loss (N) edges of Zr, providing valuable insights into its oxidation states. Complementing this, EDX offers a deeper understanding of the diffusion behaviors of heavier metals such as copper (Cu) and zirconium (Zr). Though oxygen quantification remains challenging, within the signal-to-noise ratio, we can assess oxygen saturation qualitatively and infer oxidation states accurately.

Our research highlights the efficacy of EELS and EDX techniques in unraveling the complex interplay of oxidation states as well as the elemental tracing across the interfaces. By elucidating the mechanisms governing Zr/CuO redox reaction, we contribute to advancing our understanding of its energetic properties. Furthermore, these spectroscopic tools offer promising applications in various fields where precise control over combustion processes is paramount for system optimization and material design. This study underscores the importance of leveraging advanced spectroscopic techniques for an in-depth characterization of materials, paving the way for enhanced performance and efficiency in reactive materials engineering.
Cutting edge solutions for time resolved in-situ microscopy.
G. Brunetti

1. JEOL (EUROPE) SAS, Croissy sur Seine - France

Since 1949, JEOL's legacy has been one of the most remarkable innovations in the development of instruments used to advance scientific research and technology. JEOL has 75 years of expertise in the field of electron microscopy.

This presentation will be focused on the cutting-edge development based on ultrafast shutter and laser injection inside the TEM column. Recently JEOL acquire IDES company and start developing technologies for transmission electron microscopes. IDES is a leader and pioneer in the field of Ultrafast and Dynamic TEM, specializing in pulsed lasers and high-speed electrostatic beam blanking and deflection technologies. These products add time resolution to the TEM's exceptional spatial resolution enabling new applications and the exploration of the dynamics of specimens across a range of very fast time scales. Here is a non-exhaustive list of the innovation we will present: EDM Basic (Electrostatic Dose Modulator) / Programmable STEM with EDM Synchrony / Luminary Micro Compact Specimen Photoexcitation System.

**Figure 1. EDM: Electron Dose Modulator.**

**Figure 2. Luminary Micro: Compact Specimen Photoexcitation System.**
Unveiling dynamics of metal/insulator nanodomains in V$_2$O$_3$ systems through variable-temperature monochromatized STEM/EELS techniques

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Taming resistive transitions in functional oxides is a promising approach for developing advanced information processing and storage systems. V$_2$O$_3$ is considered as a prototypical system of the metal-to-insulator transitions (MITs) where they can be activated under temperature (T), pressure, or chemical doping$^1$. When cooled below 160 K, V$_2$O$_3$ presents in parallel an abrupt MIT and a structural transition with a 1.4% volume change. This T-driven MIT has been extensively studied at the macroscopic scale$^{[2,3]}$ but also demonstrates the cautions when it comes to accurately mapping the switching dynamics of nanodomains by combining different instruments. Hence the need to perform structural and electronic experiments within the same instrument under in situ conditions and down to the nanoscale.

The electronic coexistence of insulator/metallic (I/M) domains and its phase separation mechanisms across the MIT were investigated down to the sub nm-scale with variable-T options and by combining highly-monochromatized EELS and 4D-STEM for structural investigations. The observation at low-T of an unexpected insulating hexagonal phase located at the I/M domain wall advocates for the presence of an analogous phase to the paramagnetic insulating phase emerging as a precursor of the metallic phase. These results suggest that the electronic degree of freedom is driving this T-activated phase transition.


Figure 1. a) Cryo-holder including the b) heating/biasing MEMS where c) the V$_2$O$_3$ lamella (inset Figure) is supported within the heating area. d) Series of low-loss EELS spectra probed upon heating to track the metallic signature at 1.1eV across the IMT. e) HAADF image acquired at 152 K within the I/M nanodomains coexistence and f) and g) the corresponding electronic maps where the I/M domain wall propagates here between 152 K and 152.5 K, respectively.
Electron energy loss spectroscopy in in-situ and operando liquid electron microscopy
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Nanoscale processes in liquids can be studied in real time using scanning transmission electron microscopy (STEM) combined with dedicated liquid cells. Electron energy loss spectroscopy (EELS) can be performed inside the STEM and thus, can allow for in situ analysis. In liquid electron microscopy (LEM), EELS has already been used to probe the thickness of liquid samples and the presence of water in graphene liquid cells using the oxygen K-edge. Core-edge EELS has been performed on individual nanoparticles in a colloidal suspension and on the aqueous solution around them, showing variations in the oxygen-bonding environment during irradiation. Thus, the use of EELS during LEM observations has shown significant potential for in situ analytical studies as well as to track radiolysis effects. However, the application of EELS in LEM has to date been severely limited by poor peak-to-background (S/B) ratio, mostly due to multiple scattering effects by the presence of thick liquid layers, which requires very high electron doses to overcome.

One major barrier to the widespread use of EELS in LEM has been the lack of control on the thickness of liquid during experiments. Very thick liquid layers and rapidly varying samples have long prevented high resolution EELS and EEL spectral images. Generally for the case of graphene liquid cells, controlling the initial thickness of the liquid layer and even the concentration of the initial solution during experiments has proven extremely challenging. Besides, operando LEM has not been demonstrated yet using graphene liquid cells. For the case of silicon nitride-based cells, the pressure differential between the solution inside the liquid cell and the microscope column typically lead to significant bulging of the membranes, producing inhomogeneous and thick liquid samples. Recently, however, microfabricated nano channels devices and in-vacuum loading methods have enabled the use of large areas of homogeneous thin liquid layers for LEM applications, which can be compatible with operando experiments.

Besides the application of in situ analytical methods, commonly encountered problems during operando LEM have to do with the challenges involved with scaling an experiment down to the nano-to-micro scale without affecting its representativeness. Indeed, the conditions needed to create bulk reactions may not be identical to those needed for nanoscale reactions. A series of novel cell designs have been recently developed to tackle some of these challenges. One common issue affecting representativeness when using aqueous electrolytes in operando LEM is the water splitting reaction at the electrodes interface, which causes formation and accumulation of gas bubbles in the confined volume of the cell. Another challenge has been the fact that electrochemical values recorded in commonly used setups feature a quasireference electrode, typically a thin film of gold or platinum. These values are not reliable as the electrochemical reference electrode on the chips may have an arbitrary and possibly unstable value. Novel cell designs proposing potential solutions provide: 1) new flow configurations for the removal of reaction products behind unwanted bubble formation in the working electrode, and 2) better control
and reading of the potential via the use of an external or off-chip reference electrode, not only a pseudo-reference electrode, providing more accurate electrochemical readings.15

Finally, another major limitation is that in situ and operando LEM experiments are critically affected by radiolysis caused by the imaging electron beam in the microscope. While the radiolysis of many materials by high-energy electrons has been extensively studied by conventional radiation chemistry methods, the radiolysis of solutions in the conditions of electron microscopes are poorly understood.16 Also, for the case of operando LEM with highly concentrated electrolyte solutions, such as those needed for Li-Ion batteries, the decomposition by the electron beam depends on the salt-solvent combination in a complex manner and working conditions should be assessed before the experiments.4

In this presentation, we will discuss the implementation of EELS for in-situ and operando LEM and some of the key challenges identified, as well as potential solutions proposed by us and by others in the community.17

References:

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(17) This research was funded by the European Union (ERC, DREAM-SWIM, project 101124066). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council. Neither the European Union nor the granting authority can be held responsible for them. HN and PM thanks the OPINCHARGE project, which received funding from the European Union’s Horizon Europe research and innovation program under grant agreement No 101104032 — OPINCHARGE. Measurements were performed using the IMN’s characterization platform, PLASMMAT.
Resistive random-access memory (RRAM) devices [1] or memristor devices [2] containing high-κ HfO₂ and Al₂O₃ dielectrics are promising candidates in neuromorphic computing. However, the mechanism behind the charge trapping behaviour remains unclear. By adopting correlative scanning transmission electron microscope - electron energy loss spectroscopy (STEM-EELS) and operando electron holography [3] in TEM, we have studied the chemical and electronic properties of the interfaces in tri-layer nanocapacitors, TiN/HfO₂/Al₂O₃/HfO₂/TiN (T-1) and TiN/Al₂O₃/HfO₂/Al₂O₃/TiN (T-2). Figure 1. (a)-(b) and (c)-(d) show the studied regions and the extracted phase maps at 6 V for T-1 and T-2, respectively. The measured phase amplitudes across the tri-layer insulators (Figure 1. (e) and (f)) rise with increased bias and appear symmetric when switching the sign of the bias, for example, 6 V and -6 V. An equivalent, uniform electric field distribution across both HfO₂ and Al₂O₃ layers is observed for both T-1 and T-2 nanocapacitors, which is due to the presence of trapped charges at metal-insulator interfaces and insulator-insulator interfaces. We have quantified their charge densities and found that their physical thicknesses, about 3 nm, correspond to the structural or chemical widths as shown in Figure 2. (a)-(b).

References:
Metal/insulator transitions in $(V_{1-x}Cr_x)O_3$ investigated by in situ monochromated STEM/EELS
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Various stimuli, such as temperature, pressure, doping, or electric fields, can induce insulator-to-metal transitions (IMTs) in Mott insulators and strongly-correlated systems as shown in Figure (a) [1,2]. The mechanisms underlying the electronic phase separation at the nanometric scale remain unknown. Given the structural and electronic degrees of freedom, a single instrument capable of probing all these features is necessary. In this study, we utilize in situ monochromatized EELS [2] and 4DSTEM micro/nano-diffraction [3] in a NION Ultra-HERMES 200 equipped with a Medipix direct detector and a HennyZ double tilt cryo-holder to investigate the temperature-driven IMT in $(V_{0.988}Cr_{0.012})O_3$. Our unique instrumental capabilities allow us to reveal the low-loss changes in electronic domains, particularly the identifying features of the PI, PM, and AFI phases, as shown in Figure (b). Furthermore, we uncover the potential coexistence of different phases [4] at low temperature, as shown in Figure (c). Our results underscore the significance of in situ high-energy resolution EELS as a valuable tool for studying IMTs in Mott insulators and strongly-correlated systems, providing new insights into the physics of this phenomenon.

References:
[5] The authors acknowledge funding from the National Agency for Research under the JCJC program IMPULSE, the program of future investment TEMPOS-CHROMATEM.

Figure 1. (a) Phase diagram of $(V_{1-x}Cr_x)O_3$ highlighting the temperature-driven IMT between the paramagnetic insulator (PI), paramagnetic metal (PM), and antiferromagnetic insulator (AFI) phases for x = 0.012. (b) EELS spectra of $(V_{0.988}Cr_{0.012})O_3$. (c) HAADF image of the structural coexistence of different phases at 77 K.
Assessing the stability of morphology and oxidation states of CeO$_2$ and Cu$_2$O nanocubes in a controlled atmosphere.

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Copper oxide is used as the active catalyst phase in many chemical reactions involving hydrogen. In these catalytic processes the Cu$^{2+}$ present at the initial state as CuO undergoes reduction and that Cu$^{1+}$ and Cu$^0$ species actually constitute the active phase.[1] In particular, when copper oxide is deposited on cerium oxide, which is able to switch rapidly and reversibly between the Ce$^{3+}$ and Ce$^{4+}$, the possible redox changes of the system are enhanced.[2]

As the active phase seems to be at the interface between CuO$_x$ and CeO$_2$ species, we have prepared two model systems: one based on Cu$_2$O Nanocubes (NC) with highly dispersed cerium oxide deposited on them, and another one with CeO$_2$ NC on which copper oxide particles are supported. As a first approach, prior to investigate the binary catalysts, a compelling understanding of the reduction of the bare counterparts, CeO$_2$ and Cu$_2$O NCs, is still missing. To this end the reducibility of these oxides has been studied in a hydrogen atmosphere by means of Identical Location STEM (ILSTEM) and using a DENS Solutions Climate holder in a double-corrected FEI Titan Cubed at 200 kV. Electron diffraction and EELS (Gatan Quantum 966 ERS) allow to trace the modifications on the model CeO$_2$ and Cu$_2$O based catalysts. The elemental mapping displayed in Figure 1 has been extracted from Ce-M$_{4,5}$ EELS fine structure showing the spatial distribution of Ce$^{3+}$ (green) and Ce$^{4+}$ (blue) at 450 °C and 950 °C. The in situ reduction triggers the formation of a reduced cerium-based shell which propagates towards the core of the nanocubes at elevated temperatures. To further investigate this phenomenon observed in the in situ nanoreactor and correlate this outcome with a conventional reactor, ILSTEM experiments will be accomplished.

In the case of Cu$_2$O nanocubes, the Cu$^{2+}$ has been proven to oxidize even at room temperature. Therefore, the behavior of the system is studied in controlled reducing and oxidizing environments. At this point, the first step to explore the combination of Cu$_2$O and CeO$_2$ will focus on the potential stabilizing effect of Cu$^{1+}$ due to the presence of CeO$_2$ nanoparticles supported on the Cu$_2$O nanocubes.

References:

Figure 1. Evolution of the reduced cerium-based shell in CeO$_2$ nanocubes studied with the in situ holder.
Quantitative measurement by STEM-EELS of the atomic density of helium inside nano-bubbles formed in irradiated tungsten.

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In the future ITER reactor the lowest part of the torus, called the divertor, will be subjected to extremely high heat and ions loads. Tungsten is the material chosen for this component because of its thermomechanical properties and high melting point. However, plasma-wall interactions and temperature cycling modify these intrinsic properties, and their evolution under irradiation is a major issue for both reactor operation and safety. Helium implantation, in particular, has been proven to significantly affect the sub-surface microstructure of tungsten and to induce the formation of nano-bubbles [1-2]. A better understanding of the fundamental mechanisms behind the formation of these pressurised nano-bubbles requires characterization of their morphology and of the density of the helium they contain.

The high spatially resolved STEM-EELS method is one of the only techniques capable of probing individual bubbles on a nanometric scale. Measurements for single bubbles are essential to achieve our goal of inventoring the total helium trapped in tungsten, as the size distribution of the bubbles is generally fairly dispersed, and the He density strongly depends on bubble size [3,4]. We aim to develop a methodology to quantify the atomic density of helium inside individual bubbles in order to study the density’s dependence on implantation parameters and bubble sizes. In the case of small bubbles (<10 nm) giving a weak He signal, statistical approaches such as multivariate analyses can be applied to extract the helium signal from the EELS spectra. Results for a single crystalline (110) tungsten sample, implanted at 400 eV at the ESRF in the INS2 set up of the BM32 beamline are presented. The applied He flux was \(1.0 \times 10^{17} \text{He.m}^{-2}.\text{s}^{-1}\) and the reach fluence was \(4.3 \times 10^{21} \text{He.m}^{-2}\). The sample temperature was maintained at 1273 K during He bombardment. The evolution of helium density and peak position with the bubble size that we measured in tungsten will be discussed and compared with those obtained previously for He nano-bubbles probed in others materials [5].

![Figure 1. EELS spectrum acquired at the center of a 15 nm He bubble observed in the HAADF STEM image on top right. The insert at bottom right corresponds to the extracted He peak.](image)

Usefulness of transmission electron microscopy and its associated techniques for the characterization of microelectronic components
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Nowadays, the use of transmission electron microscopy in microelectronic field enables to address accurate physical and chemical characterization or even to determine the root cause of an electrical failure. Indeed, this instrument allows to perform several types of chemical analyses owing to different spectrometers fitted with. We will describe, here, how TEM can address certain issues specific to microelectronic components. For instance, the description of the chemical order will be addressed by EDS or using other associate technique such as the Electron Energy Losses Spectroscopy which aims to provide elemental and chemical information [1, 2]. In this present work, several specific cases will be presented to demonstrate how EDS can reveal a low rate of dopants and how EELS permits to point out specific oxidation (Fig.1). In particular, a study aimed to reveal the oxidation state of copper at Cu/SiO2 hybrid bonding interface [3]. EELS investigations of the fine structure clearly revealed a self-formed Cu2O barrier for the Cu/SiO2 hybrid bonding integration. Furthermore, combining the spatial resolution of TEM and the acquisition of EELS fine structure mapping, allows to precisely measure an ultrafine copper oxide layer of only a few nanometers thick [4].

In some cases, an electrical failure could be related to a local strain. To succeed in revealing this strain, High Resolution TEM followed by GPA post-processing enables to evidenced local defects such as dislocations. Nevertheless, HRTEM imaging requires a limited field of view which also implies that the reference area is established in close proximity to the defect and is consequently strained as well. To overcome this challenge, Precession Electron Diffraction is employed to capture a wider field of view, allowing for the identification of extended defects.

References:

Figure 1. High Resolution TEM of an Ti/Al interface and EELS spectra at Al K edge.
**In situ** TEM study of the dynamic behavior of Pd-based multimetallic particles for H\textsuperscript{2} storage  
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Palladium has been widely studied for hydrogen storage, since it adsorbs hydrogen at ambient pressure and temperature.\textsuperscript{[1]} Environmental TEM studies have permitted to investigate the dynamic behavior of Pd at the nanoparticle level, revealing for instance the size dependence of H-adsorption in Pd nanocubes.\textsuperscript{[2]} Recently, bi-metallic core-shell nano-particles, such as PdIr and PdPt, have been found to have remarkable H adsorption properties compared to pure Pd.\textsuperscript{[3]} Ensemble techniques such as XRD and NMR have shown evidence of re-structuring and alloying occurring during H adsorption.\textsuperscript{[3,4]} In situ TEM, that would allow to complement these ensemble studies with local imaging and spectroscopic characterization such as EELS, has somehow lagged. In this oral contribution, we present the comparative **in-situ** study of different core-shell Pd-based multimetallic particles towards H adsorption: bi-metallic PdIr and PdAg, tri-metallic PdAgIr, and penta-metallic PdAgIrPtCu. The changes in the crystalline phase, size, and morphology as a function of hydrogen partial pressure were followed to detect phase transition and to build isotherms for individual nano-objects. These comparative **in situ** measurements on single particles allow to correlate the core and shell thickness and composition with their re-structuring, alloying, and width of the hydrogenation hysteresis.

**References:**

Acquiring time-series (or in-situ) EELS data allows for fractionating the electron dose over many data acquisitions, which are then parsed and summed to obtain the desired accumulated dose. Often, the critical dose threshold for a given material is unknown. While acquiring data from dose-sensitive specimens such as biological cells, polymers, and ceramics, the ability to save time series allows the removal of compromised data and only keep those acquired from the sample in a pristine state. The readout noise of traditional EELS detectors hinders this approach, but the new class of counting direct detection cameras are ideal for the method. The high-speed of these cameras even allows the extension to time series (or in-situ) spectrum images for combined spatial, spectra and temporal analysis.

Here, we demonstrate how in-situ spectrum imaging can be utilized to moderate the total dose to a sample over time and how it can be used to monitor changes to a sample by observing changes in the ADF images and ELNES shapes. We will demonstrate how in-situ spectrum imaging can moderate sample damage, obtain a high spatial resolution, and detect weak spectral signals in dose-sensitive samples. Calcium carbonate (CaCO3) nanoparticles are used as a model system as the total dose thresholds for reduction and mass loss are well characterized [1]. Through in-situ spectrum imaging, we were able monitor the positions of the $e_g$ and $t_{2g}$ peaks of the Ca L$_{2,3}$ edge to study how radiolysis drives the phase change from CaCO$_3$ to CaO (Figure 1). Polymer-based materials are extremely dose-sensitive and undergo phase changes at low total doses of 100-1000 e-/nm$^2$. We show that using the K3 counted camera with in-situ spectrum imaging doubled the resolution of ELNES phase mapping in a polystyrene-acrylonitrile polycarbonate polymer blend compared with a previous study that used a CCD-style camera to acquire EELS spectrum images [2]. Finally, we plan to show how in-situ spectrum imaging can moderate the dose over long acquisition times when acquiring weak spectral signals from transition metal K-edges.


Figure 1. (a) Extracted Ca L$_{2,3}$ ELNES (Edge) from pristine CaCO$_3$ (b) and after a total dose of 1.01e5 e-/Å$^2$. Gaussian functions were fitted to each peak (1-4) using NLLS fitting. The split in the L3 and the L2 edges, as well as the L2/L3 edge intensity ratio, are calculated in (c,d) using the fitted parameters from Gaussians shown in (a).
New insights into optical property characterization of 2D semiconductor materials through time-correlated photon/electron spectroscopies

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The optical properties of luminescent materials are intricately tied to their structural and chemical characteristics at the nanometric, or even atomic scale. Understanding this relationship has long relied on the combination of scanning transmission electron microscopy (STEM) with external optical techniques such as absorption or photoluminescence spectroscopies, probing the excitation and emission mechanisms at the micrometric scale. However, the significant gap in spatial resolution between these methods and phenomena of interest often leads to ambiguous or even impossible interpretations of the measurements.

Recent advancements in nano-optics seek to address this resolution disparity by enabling observation of luminescent material properties at nanometric scales. In that sense, STEM has undergone substantial instrumental and theoretical progress, providing valuable insights into optical properties through conventional inelastic electron scattering (electron energy loss spectroscopy, EELS) and photon emission (cathodoluminescence, CL) spectroscopies [1]. However, both techniques are hindered by spectral resolution limitations and the broadband excitation process of the electron beam. To overcome these challenges, two techniques currently in development will be highlighted in this contribution:

- **Cathodoluminescence Excitation Spectroscopy** (CLE, Figure 1b), based on coincidence measurements between EELS and CL events. CLE offers insights into energy transfer pathways and excitation lifetimes at the nanometer scale, as previously reported [2,3].

- **Electron Energy Gain Spectroscopy** (EEGS, Figure 1c), an extension of the photon-induced near-field electron microscopy (PINEM) technique, investigates primary electron acceleration when the beam interacts with a strong optical field generated by a laser. By changing the energy of the photons, this technique can resolve ultra-fine optical resonances in the sub-meV range, revealing novel physical properties below the energy resolution achievable with state-of-the-art monochromated electron beams. So far, it has only been applied to photonic excitations, such as plasmons or surface polaritons [4].

These techniques, with their distinct excitation and deexcitation processes (Figure 1a), are expected to be highly complementary, offering deeper insights into optical mechanisms at the nanometer scale. The present contribution focuses on using transition metal dichalcogenides (TMDs) as a model system of functional luminescent material to explore the insights provided by these correlated techniques.
Figure 1. Illustration of correlated photon/electron spectroscopies principles. (a) Band diagram schematic of excitation processes comparing cathodoluminescence excitation spectroscopy (CLE) and energy electron grain spectroscopy (EEGS). (b-c) Experimental set-ups developed at the Orsay laboratory for CLE [2] and EEGS [5] spectroscopies, respectively.
Probing optical field chirality with fast electron spectroscopies
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Chirality has a clear geometrical interpretation for massive objects such as snail shells or molecules: the impossibility of superimposing an object with its mirror image. This definition is usually encompassed in the terminology “Kelvin chirality”.

Over the last decades, a dense corpus of nano-optical experiments has reported several dichroic behaviors i.e., different responses of an optical system as a function of the handedness of the illumination. These dichroic effects – e.g. the chiral Purcell effect [1] – have motived several theoretical works aiming at extending the concept of chirality to electromagnetic fields, thus leading to the recent discovery of optical chirality [2]. Arising from a fundamental duality symmetry of the electromagnetic field, optical chirality and its flow (called spin density) obey a conservation law, as stated by Noether’s theorem [3]. Despite the extensive study of this problem over the last years, several conceptual tensions remain over its definition and properties, especially in presence of dissipative media [4]. Additionally, since all-optical techniques are constrained by the diffraction limit, there is still a lack of a versatile tool to probe chirality of optical fields down to the relevant scale i.e., the nanometric scale.

To address these problematics, we developed a theoretical framework based on earlier works on fast electron spectroscopies i.e., phase-shaped electron energy-loss spectroscopy (pEELS, [5]), polarization-resolved electron energy-gain spectroscopy (pEEGS, [6]) and polarization-resolved cathodoluminescence spectroscopy (pCL). In particular, we have demonstrated that a combination of pEELS, pEEGS and pCL enables the measurement of the optical spin density both in the near- and far-field regions, and allows to track down the microscopic origin of most of chiro-optical phenomena. In addition, this new experimental framework motivated a new definition of optical chirality based on the full and radiative electromagnetic local density of states (EMLDOS, [7]).

In this conference, we will present this new theoretical framework and especially the link between optical chirality, spin and EMLDOS. We will illustrate our finding with a comprehensive numerical investigation of the Born-Kuhn system [8] with a combination of pEELS, pEEGS and pCL, see figure 1.

References:

Figure 1. (a) 3D representation of the BKS structure. Dichroic maps for the bonding mode (745nm) of a gold BKS structure for (b) pEELS, (c) pCL and (d) pEEGS.
Transition metal dichalcogenide (TMD) monolayers and their van der Waals (vdW) heterostructures have garnered significant interest following the observation of bright photoluminescence [1]. Their high exciton binding energy and spin-orbit splitting make them promising candidates for optoelectronic applications.

In this contribution, we discuss the advancements in understanding TMD van der Waals heterostructure nano-optics using electron spectroscopies in scanning transmission microscopes (STEM), achieved over the last five years at LPS-Orsay. We begin by describing the initial STEM-CL experiments conducted on h-BN encapsulated TMD monolayers [2], which followed the seminal SEM-CL work by S. Zheng [3]. Spatially resolved STEM-CL demonstrated that trion emission could be localized down to the tens of nanometer scale (Figure 1). In h-BN encapsulated heterostructures, EELS excitonic transitions are as narrow as those in optical experiments conducted at the same temperature, prompting a survey of different substrates [4] to understand the role of h-BN. Continuing with EELS, we examined the influence of the twist angle between two WSe$_2$ layers on excitonic transitions [5]. We observed a shift in the C exciton transition as a function of the twist angle, which was interpreted using first-principle calculations [5]. Lastly, by encapsulating TMD monolayers on thin graphite and graphene, we demonstrated that excitonic transitions exhibit a Fano-like line shape, contrasting with the Lorentzian line shape observed for free-standing and h-BN encapsulated monolayers [6].

References:

Figure 1. a-b CL filtered maps and spectra of an h-BN/WS$_2$/h-BN heterostructure [2]. c EELS spectra of MoSe$_2$ encapsulated in graphite and h-BN. An asymmetric line shape is observed for graphite encapsulation [6].
Resolving local chemical and atomic arrangements in Carbon Nitrides using EELS

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Carbon nitrides (C₃N₄) attract a lot of attention for various applications in the areas of catalysis, water remediation, and energy supply and storage [1]. Their performance often relies on the precise control of the chemical composition, atomic and electronic structure at the nanoscale. As many of C₃N₄ are poorly crystalline or even amorphous, often radial distribution functions (RDFs), obtained using data from total scattering or absorption spectroscopy experiments at a synchrotron, are used to analyze their structure. Similarly, (S)TEM can be employed, namely analysis of RDFs from both electron total scattering data and EELS data within from the same area of the specimen. The easy access to TEMs in different laboratories makes this approach a powerful tool to screen and analyze a lot of samples prior to synchrotron studies.

Here we applied a combined analysis of RDFs obtained from electron diffraction [2] and EELS data [3] to soft polymeric materials. We used two challenging C₃N₄ systems to sense the limits of our approach: (1) ability to distinguish between two structurally close polymeric materials; (2) ability to sense the local environment around single-atom catalysts. In this abstract, we focused on RDF analysis of spectroscopy data.

1. Samples of PTI, K-PHI and a heterojunction between them were analyzed [4]. EXELFS signals from N K-edge were collected at different voltages and at cryo-conditions to optimize the EELS signal and reduce electron beam damage. RDFs enabled sensing local chemical environment up to the 4th coordination sphere of nitrogen. First three distances are identical in PTI and PHI. The fitting of RDFs obtained from individual phases and the heterojunction is in progress.

2. We analyzed 4 Ce-doped C₃N₄, with different Ce loading primarily tested for photocatalytic wastewater dephosphorylation, the position and the intensity of the first peak on RDFs obtained from Ce M₄,5-edge of the best-performing sample suggest that Ce binds to C or N and mainly forms single atoms. The combined analysis of EXAFS and EXELFS is currently in progress and should help us to evaluate amounts of different fractions (single atoms, clusters and CeO₂ particles) in these samples, explaining the difference in efficiency of photocatalytic dephosphorylation.

References:
5. Max Planck Society is gratefully acknowledged.
Applications of frame-based and event-based hybrid pixel electron counting in EELS

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Hybrid pixel electron counting detectors offer many advantages in electron microscopy. From direct imaging and separation of background noise sources to digital readout, this technology allows the detection of single electrons on an otherwise dark background with zero counts. Electron counting within each pixel of the detector can be done with sufficient speed to detect relatively intense probes, such as the zero-loss peak or focused parallel electron diffraction patterns. An additional feature these detectors uniquely bring to electron microscopy is a true zero-suppressed signal and highly accurate time-stamping of each detected event. Because of these advantages, hybrid pixel detectors have enabled novel applications and have been used to advance many areas of transmission electron microscopy.

This talk will focus on EELS applications of frame-based detectors (MerlinEELS, Cheetah M3) and event-based detectors (Cheetah T3). The enabling technologies for these detectors are the Medipix3 [1] and Timepix3 [2] chips developed at CERN. We will explain the frame-based and event-based approaches in EELS and demonstrate the advantages they bring to the field.

References:
Poster contributions
Electronic properties of 2D Transition Metal Dichalcogenides ternary alloys: an ab initio study
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First principles calculations are performed to investigate the properties of monolayer transition metal dichalcogenides (TMDs) ternary alloys of the form MXY, with M = Mo, W and X̸= Y = S, Se. We are particularly investigating the influence of the composition of these alloys on the evolution of the band gap. To have a better understanding of the composition dependent, the thermodynamic stability, structural and electronic properties of these alloy configurations at various concentrations have been comparatively studied using the density functional theory (DFT). We found that the introduction of the foreign Y atom affects the lattice constants of the 2D systems, in agreement with literature [1]. From bandstructure analysis, we saw that the introduction of the Y chalcogen fine tune the band gap of a MX 2 monolayer keeping the direct band gap at K point. The partial density of states analysis reveals that the band gap is mainly due to the d orbital of M atom and the p orbitals of X atoms. Beyond these ground-state properties, the electronic density, and the Kohn-Sham structure of studied systems are used to calculate the absorption and electron energy loss spectra, within time-dependent density functional theory (TD-DFT) using the Selected-G method [2]. The spatial dependence of the response function as well as of the induced density are also analysed [3]. Our results show clearly specific signature of the electronic density for each chalcogen.

References :


Figure 1. EELS in-plane (blue) and out-of-plane (red) for MoSSe monolayer.
In situ electron beam irradiation of Ti$_3$C$_2$T$_2$ MXenes. A STEM-EELS study

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MXenes are a family of 2D transition metal carbide or nitride layers obtained from the exfoliation of nanolaminated ceramics called MAX phases [1]. Their chemical formula is M$_{n+1}$X$_n$T$_z$ (n = 1, 2 or 3), with M a transition metal, X being C and/or N, and T are surface terminations (e.g. O(H), F, Cl) inherited from the exfoliation process. They present very good electrical conductivity, as well as high hydrophilicity, making them very promising materials for various applications, including transparent conductive electrodes or energy storage devices [2]. A previous study [3] showed the strong influence of ion irradiation induced defects on the structural and physical properties of MXenes, resulting in a reduced hydration potential, an increase in the charger carrier density as well as modifying their optical properties, all the while maintaining a stable conductivity.

In this context, we present a new approach to defect engineering in MXenes, using electron beam irradiation in situ, in a transmission electron microscope (TEM), performed in cryogenic conditions. This is achieved by adjusting the exposure time, the beam current and the number of frames in STEM-EELS (electron energy-loss spectroscopy) measurements, to reach an electron dose that allows for the introduction of defects into the sample. This is a highly controllable technique, which results in the creation of either punctual holes, roughly the size of the electron beam, or bigger “crater-like” holes spanning over hundreds of nm$^2$, depending on the irradiation conditions. Moreover, the EEL spectra acquired, both during and after irradiation, allows us to follow the evolution of the structure and chemistry of the sample, as a function of the electron dose. This innovative approach can potentially be generalized to other MXenes and 2D materials, as well as up scaled to thin films using other electron irradiation techniques such as SEM.

References:

Figure: (a) STEM micrograph showing the irradiated region circled in white. The blue rectangle indicates the series of line profiles presented in (b), showing the depth and width of the irradiation induced hole. (c) A comparison of EEL spectra measured on pristine and irradiated areas of the same region.
Eu³⁺-doped Y₂O₃@SiO₂ core@shell structures: a comprehensive study on the formation of Y₂SiO₅ hollow spheres

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Luminescent rare earth (RE³⁺)-doped nanoparticles (NPs) have been explored as multifunctional materials for biological and medical applications, including bioimaging, photodynamic therapy, and temperature sensing [1,2]. In this sense, some of us have reported luminescent spherical and monodisperse Er³⁺,Yb³⁺ co-doped Y₂O₃ NPs with view for application as optical markers and nanothermometers aiming their use as a new therapeutic and diagnosis platform against brain cancer and other cancer diseases [2]. To enhance the biocompatibility, core@shell Eu³⁺:Y(OH)CO₃@SiO₂ NPs were prepared. First, yttrium hydroxycarbonate was prepared by homogeneous precipitation via urea thermolysis, giving NPs with 100 nm mean size. Then, a homogeneous silica shell was deposited through the Stöber method, varying the tetraethyl orthosilicate (TEOS) amount based on the Y:Si (m/m) ratio at four concentrations (1:1, 1:2, 1:5, and 1:10). It was observed the formation of Y₂O₃:RE@SiO₂ or Y₂SiO₅/Y₂O₃:RE@SiO₂ after the annealing at 900 °C for 2h (confirmed by XRD), as well as morphological changes and a hollowing phenomenon observed by TEM (Figure 1) and HR-TEM (Figure 2). After annealing, nanovoids arose in the center of the nanoparticles. We could follow the increase of the SiO₂ thickness layer by EDX analysis. With the increasing of the shell layer, we obtained the monoclinic Y₂SiO₅:Eu³⁺. Eu³⁺ ions can be used as structural probes and their luminescence spectra was used as a tool to follow these structural changes. The emission spectra profile and the ⁵D₀ lifetime values considerably changed when compared to the Y₂O₃:Eu. These hollow spheres can play essential roles in various applications due to the presence of an empty space or void inside, such as for drug delivery and phototherapeutic applications in nanomedicine.

References:

[4] We acknowledge FAPESP, CAPES, and CNPq.
Figure 1. TEM images of Eu$^{3+}$:Y$_2$O$_3$/Y$_2$SiO$_5$@SiO$_2$ hollow spheres varying Y:Si (m/m) ratio, for sample a) 1:1, b) 1:2, c) 1:5, and 1:10 samples annealed at 900 °C for 10h.

Figure 2. High-Resolution Transmission Electron Microscopy (HR-TEM) images of Eu$^{3+}$:Y$_2$O$_3$/Y$_2$SiO$_5$@SiO$_2$ hollow spheres 1:10 Y:Si (m/m) ratio sample annealed at 900 °C for 10h.
Structural and chemical study of interfaces in TiAlN/TiAl multilayers
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Nanocrystalline metallic nitride coatings are currently used for their outstanding properties: hardness, good wear resistance, thermal stability by improving oxidation resistance, which make them attractive as protective coatings. To improve fracture toughness while maintaining a high hardness, TiAl/TiAlN metal/nitride multilayered coatings, were deposited by magnetron reactive sputtering technique named Reactive Gas Pulsing Process (RGPP) [1], allowing to modulate the layer’s composition by pulsing the nitrogen reactive gas. This technique allow to take advantage of the properties of the nitride (covalent hard material), the metal alloy (ductile layer) [2] and the crack resistance of the interfaces [3]. Multilayered films with different period in a range of 4 to 50nm, were deposited by RGPP, for a total coating of 1500nm.

The role of the composition, thicknesses of the two nano-layers as well as the interfaces, on the mechanical behavior of the film, is crucial that is why the study will focus on the chemistry and structural properties at the atomic scale before and after nanoindentation tests. This will be studied by combining Energy Dispersive Spectroscopy and Electron Energy Loss Spectroscopy as well as conventional Transmission Electron Microscopy, all along the stack.

References:

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Figure 1. ADF STEM image and N and Ti mapping of a selected area.
EELS Spectra classification: Machine Learning vs Neural Network

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Processing EELS spectrum-images can be challenging, as it involves mapping changes in the fine structures of core-loss edges in transition metal oxides. These subtle changes, which can be probed at the atomic scale in STEM-EELS, reflect the interplay between the valence states of the transition metal and its crystal structure, thereby affecting the physical properties of the oxides. Various methods are employed for this task. Some, like Principal Component Analysis (PCA) and Non-negative Matrix Factorization (NMF), decompose each spectrum at a sub-pixel level. Others, such as clustering, assign unique labels to every pixel. Clustering has been utilized in EELS data processing through algorithms like K-Means, hierarchical clustering, and DBSCAN [1-3].

Recently, Neural Networks have been used for EELS spectra classification using an Autoencoder-Classifier (AEC) [4]. This method, which requires a training dataset, focuses on variations in fine structure.

Our objective was to evaluate the AEC approach against traditional Machine Learning (ML) methodologies. We analyzed the fine structures of the Co-L\(_3\) edge in Co\(_3\)O\(_4\), a model system. This system was chosen because it presents Co\(^{2+}\) in tetrahedral coordination and Co\(^{3+}\) in octahedral coordination, with these different sites spatially separated by 1.9 angstroms along the [110] zone axis.

We simulated a dataset with Co\(^{2+}\) and Co\(^{3+}\) presenting fine structure variation of the L\(_3\) edge. The performances of different clustering algorithms were compared to that of the AEC under varying noise levels. Our findings indicate that these methods have comparable performance, with ML methods being more straightforward to implement.

References:


Fig. 1: a) t-SNE plots of simulated spectra at varied SNR values and of corresponding experimental spectra labeled with K-means. b) individual spectrum corresponding to different SNR c) simulated L\(_3\) edges.
EELS contribution to the study of VO$_2$ electrochromic films.
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Electrochromism is a modulation of the optical properties under an applied voltage. This property is of great interest for the scientific community and a major challenge is the discovery of new appropriate materials. In this study, multi-electrochromism is described from VO$_2$ thick films. Thanks to a collaboration via METSA network, a complex mechanism based on the oxydo-reduction of the vanadium cations and the strong memory effect in oxides are presented. Upon cycling, a progressive reversible switch occurs: the film color change from orange-V$_2$O$_5$ on oxidation to green and blue in reduction which illustrates a mixed vanadium oxidation state.

References:


**Figure 1.** Evolution of the cyclic voltammograms (1, 20 and 50 cycles) of VO₂ film cycled in Pt/LiTFSI-EMITFSI/VO₂ vs SCE with a 10 mV/s scan rate and visual appearance of the films in different color states.

![Graph of cyclic voltammograms](image)

**Figure 2.** High-resolution TEM images of VO₂ film after 50 cycles at reduced green state (a), reduced blue state (b) and reoxidized orange state (c) and corresponding Selected Area Electron Diffraction patterns: d, e, f.

![TEM images and diffraction patterns](image)

**Figure 3.** EELS spectra of VO₂ film as-deposited and after 50 cycles at reduced green state, reduced blue state and oxidized orange state. V-L₃ : 513 eV, V-L₂ : 520 eV, O-K : 532 eV.

![EELS spectra](image)
Free electron spectroscopy seen through the prism of quantum optics
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Photon Induced Near-field Electron Microscopy (PINEM) denotes the modulations of free electrons by a sample – typically an optical cavity – pumped by a laser source. This effect has been theoretically predicted and experimentally demonstrated in an ultrafast transmission electron microscope (UTEM) more than a decade ago [1,2]. Following these seminal developments, PINEM has been used to reconstruct the temporal dynamics of nano-optical systems with an attosecond temporal resolution [3]. Due to recent experimental developments in integrated photonics [4,5], the problem of PINEM in the low occupation regime – i.e. when the cavity is populated by a weak number of photons - has drawn an increasing theoretical interest. Indeed, in this situation, the classical description of the electromagnetic field falls short to describe the electron-cavity interaction, and a full quantum description becomes required. Several works have already pioneered this problem [6,7] and predicted strong quantum mechanical effects in PINEM.

The goal of our work is to pursue this effort and provide an alternative and intuitive approach to this problem by using tools borrowed from the field of quantum optics. Especially, we have extensively used the Wigner function - roughly speaking, a probability distribution of the electron in the phase space (energy-time) – as a powerful visualization tool, as shown on figure 1.

In this contribution, we will introduce our approach and demonstrate its efficiency on several problems. In a first part, we will illustrate the influence of the quantum optical state of the cavity (e.g. Fock states, coherent states, squeezed states) on the energetic and temporal structure of the electron beam during the PINEM interaction. We will show that a PINEM measurement in this regime is deeply connected to the standard quantum limit to the temporal resolution in a UTEM. In a second part, we will tackle the question of the quantum to classical transition in free electron scattering and show that the Wigner function elegantly highlight the transition between the stimulated and spontaneous scattering regimes in electron energy-loss spectroscopy (EELS). Eventually, we will apply our approach to several experimentally achievable situations such as the probing of quantum emitter-cavity coupling in EELS.
Figure 1. Electronic Wigner function after interaction with (a) a classical electromagnetic field and (b) a quantized electromagnetic field. The Wigner function (central panel) provides a direct visualization of the energy distribution (right panel) and the temporal modulation (top panel) of the electron at the same time.

References:
CLE for studying quasi-particle excitations and the quest of suppressing transition radiation

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Cathodoluminescence excitation spectroscopy (CLE) in Scanning Transmission Electron Microscopy (STEM) is a technique that correlates electron excitation with subsequent photon emission events. These are measured via electron energy loss spectroscopy (EELS) and cathodoluminescence spectroscopy (CL) respectively and correlated via nano-second resolved coincidence detection using a Timepix3 detector for electrons and PMTs for CL. A crucial difficulty with electron spectroscopies is the broadband nature of the electron-matter interaction, which prevents the controllable creation of excitation at a predetermined energy. Therefore, a time-resolved setup that allows for the tracking of which excitation energy leads to a photon emission (Figure a)) is required. CLE has the added benefit to follow excitations’ life span from creation to decay into photons with nanometer spatial resolution [1]. Our research utilizes CLE to investigate single point defect emitters in nanomaterials. We currently focus on defects in hexagonal Boron Nitride (hBN) and diamond nanoparticles. However, the high sensitivity of CLE also picks up other signals, notably transition radiation (TR), which occurs in an energy range overlapping with in-gap excitations we aim to measure [2]. Thus, we are currently working on filtering out the contribution of TR using spectral, spatial and possibly temporal approaches.


Figure: a) Schematics of electron-photon coincidence detection for CLE. b) EELS spectrum (purple) and CLE spectrum (blue) of hBN, the latter showing TR. Reproduced from [1].
AI Automation for Transmission Electron Microscope Alignment
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Transmission Electron Microscopes (TEM) require precise alignment of many components to allow microscopists to get precious information on their samples. This is traditionally done by hand, although algorithms are being developed for some of these processes [1]. It still takes microscopists dozens of minutes daily and makes the instrument harder for beginners to use. To tackle this difficulty, we propose to rely on Artificial Intelligence and especially CNN’s [2] to automate this process. We tested it on automatic aperture alignment and are trying to implement it for full TEM alignment on a modified Hitachi HF3300. In the future, this could be used to automate the alignment of other instruments connected to the microscope such as the spectrometer used in EELS.

\textbf{Methods}
We first took control of all the microscope’s components through a Python application. Then the goal was to use a CNN model to modify the microscope’s configuration for each step of the alignment process. We focus here on the first step, condenser aperture alignment. We created a dataset linking images to the corresponding shift of the aperture position to correct it. We aligned the microscope manually and then changed the position of the aperture by a known displacement before taking seven images at varying condenser lens values. This is done to simulate a wobble and gives the necessary information to do the correction. Then we associated this image with the corresponding displacement and by repeating the process constituted the dataset. This dataset was then used to train a CNN network to predict the displacement based on the stack of images.

\textbf{Results and perspectives}
The resulting model allowed us to predict the aperture displacement with human accuracy with only 15 seconds of acquisition (Fig. 1). The concept could be applied to other microscopes or instruments. In addition, it could be adjusted to address difficulties such as spectrometer alignment by training on the spectrometer output to make the zero-loss peak as sharp as possible. The goal is to incorporate the entire solution into an application that allows microscopists to use the automation functions seamlessly while making it simple to create or strengthen automation routines.


\textbf{Figure 1.} Aperture alignment example.
Cationic ordering in natural spinel structures

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The spinel group minerals appear frequently in rocks and their large compositional ranges make it an important tracer of the conditions under which the spinel and its bearing rock have crystallized [1,2]. Within the spinel structure oxygen atoms are organized in a cubic close-packed lattice forming tetrahedral (T) and octahedral (M) sites where heterovalent cations reside. The structural chemistry of spinels can be described as \((A_{1-x}B_x)^2(\text{Fe}_{1-x}B_{2x})_3\text{O}_4\) with \(x\) being the inversion factor. In normal structure \((x=0)\) tetrahedral sites are occupied by divalent cations and octahedral site are occupied by trivalent cations. The cation distribution and the degree of inversion can however highly vary depending on the crystallization conditions. The degree of disorder over T and M sites is usually studied by macroscopic approaches such as x-ray diffraction [3] and Mössbauer spectroscopy [1,2]. Precession electron diffraction has also been applied for the retrieval of the ordering state in orthopyroxene [4].

In this study we use core loss STEM-EELS spectroscopy to obtain site specific spectroscopic information and attempt to decipher the charge and chemical degree of order between the tetrahedral and octahedral coordination within magnetite \((\text{Fe}_3\text{O}_4)\) and MgFeAl₂O₄ crystals found in the Martian NWA7533 and the Allende meteorites, respectively. We address challenges such as beam damage and low signal-to-noise ratio through a multi-frame acquisition approach using a direct electron detector. Our first results indicate that octahedrally coordinated Fe cations are partially divalent and the octahedral sites within MgFeAl₂O₄ are Al-rich. Within this study we aim to quantify deviation from stoichiometric concentrations of the nominal \(\text{Fe}^{2+}/\Sigma\text{Fe}\) and Mg/Al ratios for the two spinel structures. Obtaining such site-specific quantified information can contribute in understanding thermal history of these two meteorites.

References:

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Figure 1. ADF images for (a) magnetite (Fe$_3$O$_4$) in NWA7533 and (c) spinel (MgAl$_2$O$_4$) in Allende meteorites. Red and blue circles indicate octahedral sites (M) and tetrahedral sites (T) respectively (b) Fe-L$_3$ spectra obtained over 16 octahedral (M) atomic columns (red lines) and 16 tetrahedral (T) atomic columns (blue line). (d) Mg-K and Al-K edges obtained over 120 octahedral (M) atomic columns (red lines) and 120 tetrahedral (T) atomic columns (blue line).
Correlating the chemical structure and plasmonic properties of bimetallic nanoalloys.

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Combining metals at the nanoscale offers opportunities to explore and fine-tune physicochemical properties for nanoparticle-based devices. Bimetallic nanoparticles (BNPs) exhibit properties influenced by size, shape, environment, chemical composition, and spatial elemental distribution. These properties can change significantly depending on their chemical configuration (alloyed, segregated, chemically ordered, etc.), affecting their optical, magnetic, or catalytic behavior [1]. Alloying noble and trivalent metals in nanoparticles has been shown to be a feasible way to shift the Localized Surface Plasmon Resonance (LSPR) further into the UV spectral range, opening the way for applications in UV photocatalysis, sensing, and the generation of high-energy hot electrons. Here we study the mixing of elements Au, Ag, and In to correlate the plasmonic response and chemical structure of bimetallic structures. As a basis for studying challenging bimetallic nanoparticle systems such as InAg or InAu, we established our methodologies for quantitative chemical analysis in a benchmark of AgAu alloy nanoparticles in the size range of 4-10 nm [2]. Going further, we investigate the chemical structure of the InAg/InAu systems using energy-dispersive X-ray spectroscopy in a STEM and separate metallic from oxidized phases using unsupervised machine learning techniques such as principal component analysis (PCA) and non-negative matrix factorization (NMF). Complementary imaging in both HRTEM and STEM-HAADF and SAED is used to characterize the metallic structures. In this context, UV-Vis and Low-Loss EEL spectroscopy are used to characterize the plasmonic response of the ensemble and single BNPs [3], respectively. Finally, by combining imaging, diffraction, and spectroscopy techniques using a TEM, we show that In₂Au is a good candidate to correlate plasmonic and structural properties as it shows an LSPR in the UV range and improved stability against oxidation compared to other alloy combinations.

Electron microscopy: an efficient tool to evaluate UCNPs complex structures for bioimaging applications.
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One of the challenges of recent years in in vivo imaging is the development of probes that are sufficiently effective for in depth exploration of biological tissue while instigating little to none biological harm. Due to the absorption properties of the in vivo terrain, the near infrared portion of the spectrum is extremely advantageous, especially for fluorescent imaging. This region is known as the maximum transparency of the biological window, i.e., good penetration depth, reduced auto-fluorescence and tissue scattering.[1] Potentially multifunctional, nanoparticles are great candidates for imaging technologies. Upconverting nanoparticles (UCNPs), Ln$^{3+}$-based NPs, are very attractive candidates due to narrow emission bands, long-lived lifetimes, and their anti-Stokes emission. Herein, we have proposed Ln$^{3+}$-based core-multishell UCNPs towards excitation and emission at 800 nm. To achieve such an ambitious goal, multilayered UCNPs were engineered, relying on the Nd-Yb-Tm triad embedded in NaYF$_4$ matrix.[2] These UCNPs were strategically designed as a three-layer structured material to prevent cross relaxations between Nd and Tm.[3] These core@multishell UCNP synthses can be complex leading to a certain uncertainty whether the desired structure was achieved or not. An accurate characterization of UCNPs architecture is mandatory to assure its photoluminescence overall performance towards an effective contrast agent for bioimaging applications. Fortunately, spectroscopic and electron microscopy techniques such as TEM, HRTEM, and EDX help to clarify the obtention of the desired architecture and composition of such NPs. Herein, we were able to exploit and confirm the generation of a high crystalline homogeneous core@multishell and heterogeneous core@shell NPs through the above-mentioned analysis. Additionally, core@shell exhibiting different sizes were characterized by these techniques to exploit the number of cores per particle according to its size. The confirmation of a Gd$_2$O$_3$S@NaYF$_4$ heterogeneous structure by several techniques is presented in Figure 1.[4]

![Figure 1](image.png)

*Figure 1.* Composition and architecture of the heterogeneous UCNP (a). HAADF STEM (b) and Gd, Tm, Yb, O, F and S element mapping.

Microcharacterization of medieval fire-gilded Cu jewellery by EDS and SAED analysis
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Previous study of fire-gilded Cu jewellery from the Early Middle Ages in Central Europe revealed micrometric Au-Hg metallic two-layer structure, with submicrometric grains forming a solid bond between the gilding and the Cu base substrate[1]. In this communication, one of these fire-gilded Cu fragments is characterised up to the nanoscale resolution applying scanning transmission electron microscopy (STEM) coupled with energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) to reveal more details of microstructure, phases and chemical distribution of the Hg amalgam gilding. Focused ion beam (FIB) milled thin TEM lamella evidence that the fire-gilding is composed mainly of Au solid solution including Cu, Hg and Ag with face centre cubic (FCC) structure (space group 225, Fm-3m). This layer is compose of different chemicals regions that are mainly organized as follows:

- an external Au layer including typical diffusion profile of Cu coming from deep layer followed by
- a Cu rich inner layer with different amount of Hg directly in contact with Cu substrate.

The microstructure of the external Au layer is made of µm grains without textural growing confirming a sintering process of Au globules rather than a columnar growing from metallic germs. On the contrary, inner layer is made of sub-µm grain which is clearly linked to Cu diffusion process of substrate. Diffraction patterns of different zones into two different layers show a lattice parameter modification of FCC structure from Cu substrate to free surface of fire-gilding.

Based on the binary and ternary systems involving Au-Ag-Cu-Hg elements, precise identification of metallic (Au fire-gilding and Cu substrate) structures, compositions and phases directly inform on the temperature applied during the heating step of the gilding technology employed. Here, results confirmed two hypothesis: heating temperature applied to the amalgam gilding was most likely above 400°C, and this high temperature induced an internal oxidation of the Cu substrate forming well crystallised cuprous oxide grains, as demonstrated by SAED analysis.

References:
Towards electron beam shaping in an Ultrafast Transmission Electron Microscope
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In 1933, Ernst Ruska developed the first Transmission Electron Microscope (TEM) which became the primary tool for studying matter. The picometer De Broglie wavelength and the numerous signals generated by an electron allow us to probe many properties of a sample at the atomic scale. Indeed, by analyzing the amplitude, phase, deflected angle and the energy of the electron beam after its interaction with the sample we can fully reconstruct its chemical composition or its magnetic/electric properties. However, unlike conventional optics, where the amplitude, phase and polarization of a light beam can be fully controlled using e.g. a Spatial Light Modulator (SLM), the electron beam cannot be easily manipulated in a TEM, making electrons insensitive to certain fundamental properties such as chirality. The development of Ultrafast Transmission Electron Microscopes (UTEM), whose working principle is illustrated on figure 1, has opened new possibilities. In 2020 it has been proposed to shape the electron beam through inelastic electron-light interactions in Photon-Induced Near field Electron Microscopy (PINEM) experiments [1] as sketched in figure 1. The PINEM interaction, based on a pump-probe experiment, relies on energy exchanges between an ultrashort electron pulse and a strong optical near-field induced on a sample by a femtosecond laser pulse. One of the main properties of this interaction is to imprint the laser beam phase on the wavefunction describing the electron after the interaction. Two years later, a first practical demonstration [2] illustrated the capability of this technique to generate Gaussian/Hermite-Gaussian electron beams.

The aim of our work is to develop an experimental set up for electron beam arbitrary shaping on a brand-new UTEM developed at CEMES [3]. This new 300 keV UTEM based on a modified Cold Field-Emission Electron Gun (CFEG) has been equipped with two sample stages that will enable us to use the shaped electron beam to probe a sample of interest. This poster will focus on the development of the optical set up and numerical simulations of the electron beam shaping capabilities.

References:
**Figure 1. Ultrafast Transmission Electron Microscope and PINEM schematics**
TEM/STEM investigations of an unexpected contrast asymmetry in topological insulator BiSb and in pure Bi
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Topological insulators form a new class of materials which attracts a lot of attention lately. These materials differ from conventional insulators in virtue of their topologically non-trivial band structure, resulting in spin-polarized surface states. The first experimental observation of a 3D topological insulator was made in 2008 on bismuth antimony alloys (BiₓSb₁₋ₓ) [1]. In a recent work [2], the MPN group at LAAS has developed state-of-the-art molecular beam epitaxy (MBE) methods to integrate epitaxial layers of bismuth antimony alloys on a GaAs substrate.

High resolution STEM-HAADF observations were done on these samples to check the growth quality, and an unexpected contrast asymmetry has been observed along the growth direction [001]. In this direction there is an alternance between a covalent bond and a van der Waals one, so that atomic planes are grouped 2 by 2. The asymmetry, as illustrated in figure 1, appears between every two columns: one column is more intense than the other. This asymmetry was quantified to 1%. This effect was observed both in BiSb alloys and in pure Bi in STEM-HAADF, which is even more surprising as HAADF presents mainly a chemical, or Z contrast.

HRTEM observations with negative Cs were recently carried out and they show the same asymmetry in pure Bi samples, this time more intense, around 15%. These observations reject the hypothesis of a chemical contrast, HRTEM being weakly sensible to chemical composition.

In parallel, multislice image simulations were conducted to try and understand this unexpected contrast. Several parameters of the simulations were modified, such as a small beam tilt or the aberrations of the microscope. Another hypothesis was to include the effect of the objective lens’s magnetic field. Indeed, bismuth high spin-orbit coupling could induce an asymmetry in the atomic potential, and consequently in the images. For this purpose, a perpendicular field of magnitude 1 T was introduced using ab initio potential calculations.

Figure 1. HRTEM image ($C_s < 0$) of a pure Bi sample in [100] zone axis, taken on the I2TEM, a CFEG $C_s$-corrected microscope. One can observe the alternating contrast between neighboring planes.
Study of nanolaser optical and structural properties at the nanometer scale

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Since their first demonstration by Huang et al in 2001[1], semiconductor nanolasers have attracted a lot of interest especially for their application in optoelectronic devices. They have the advantages to be cost-effective, easy to fabricate and of a micron size. Since 2001, various semiconductors and geometries demonstrated lasing properties, for example ZnO[1] or GaN [2] nanowires act as nanolasers. Lasing could be induced by optical pumping, usually it is characterized by a drastic reduction of the emission spectrum width, increase of the light coherence evidenced by interferences of laser diffracted light. The most significant lasing properties of nanolasers are the value of the lasing threshold, the emission wavelength and the reduction of the carrier lifetime. Moreover, nanolasers emission wavelength above the lasing threshold are linked to the laser cavity's resonance modes, which in our case is the nanowire itself. Thus, the shape of the nanowire and the laser characteristics are closely related. Due the nanoscale variation, electron microscopy is a suitable technique to examine its nanoscopic characteristics. Therefore, it is essential to link the lasing properties with the nanolaser shape and the local luminescence.

We particularly focused on the use of cathodoluminescence in a scanning electron microscope (SEM) and a scanning transmission electron microscope (STEM) to characterize the optical properties of GaN nanowires. In both microscopes, the focalised electron beam locally creates charge carriers in the semiconductor, in a pair of interaction of either hundreds of nanometers (SEM) or tens of nanometers (STEM). We studied the luminescence due to carriers recombination. Using a spectrometer, we can obtain a spectrally resolved map of the sample emission. In time-resolved electron microscopy, we are able to measure the charge carrier lifetime thank to the decay curve of the luminescence after an electron pulse (30 ps in SEM and 300 fs in STEM). In this project we measure the lasing threshold and the cavity mode of single nanolasers and correlate the results to their nanoscale geometry and optical properties using cathodoluminescence and time-resolved cathodoluminescence measured both in STEM and SEM.

References:
Figure 1: a.b. TEM bright field image of a nanolaser c. SEM Secondary electron image of the nanolaser studied in cathodoluminescence in d-h d. Nanolaser intensity map extracted from the time resolved cathodoluminescence dataset e. Time-resolved cathodoluminescence decay trace at different points of the nanolaser (shown in d) f. Cathodoluminescence intensity map of the nanolaser at 368nm with a bandwidth of 10nm g,h. Cathodoluminescence spectra at different positions on the nanolaser (shown in f)
Structural, chemical and magnetic correlations of chromite epitaxial thin films

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The Fe-Cr-O ternary system, known as chromite, can have applications in diverse disciplines such as geology, metallurgy, corrosion, and spintronics. Among 3 different crystallographic structures, the spinel one (Fe$_3$-xCrxO$_4$) is a mixture of divalent and trivalent cations within a cubic MgAl$_2$O$_4$-type framework. Multivalence cations arrange within a geometrically intricate network of octahedral (Oh-sites) and tetrahedral (Td-sites) sites. This structural complexity offers ways for tailoring functional properties like magnetization, Curie temperature, and electronic transport by introducing various metal cations into the host matrix. For example, substituting Fe cations with Cr in magnetite transforms the half-metal host ferrimagnet into either a semiconductor or an insulator, depending on the x values.

This study presents a thorough investigation into how compositional properties influence the structural and epitaxial characteristics of Fe-Cr-O thin films. The thin films were fabricated using oxygen-plasma-assisted molecular beam epitaxy (O-MBE) on single crystalline α-Al$_2$O$_3$(0001) substrates. As a result, epitaxial growth of 15nm thick Fe$_{3-x}$Cr$_x$O$_4$(1 1 1) thin films with high crystalline quality were achieved.

Stoichiometric series of epitaxial Fe$_{3-x}$Cr$_x$O$_4$(111) thin films were prepared with x varying from 0 to 1.7. The chemical and structural properties of these different layers were investigated by TEM related techniques and compared to XAS, XPS and XRD for instance. The magnetic properties, measured by XMCD, were correlated to the organization of the chemical species in the layers.

References:

Figure 1. High resolution TEM image and associated RHEED patterns of Fe$_{2.8}$Cr$_{0.2}$O$_4$ films (left), and Fe$_{1.6}$Cr$_{1.4}$O$_4$ films (left)
In this work [1], we put our focus on an in-depth understanding of the oxidation mechanism of titanium within a thermite system by employing a magnetron-sputtering technique to grow high purity and well-defined CuO/Ti reactive thin film (RMF), which features a very well-controlled interface (in thickness and structure) between the fuel and oxidizer. The multilayer system allows full contact between the different species compared to the particle system shows random contact, which is crucial to identify and rationalize the different mechanisms taking place during reaction. This provides an ideal model system to describe the TiO$_x$ interfacial oxide growing quantitatively.

An RMF containing four nanolayers, CuO/Ti/CuO/Al, was prepared and annealed at 300 and 500 °C, respectively, and then studied using high-resolution electron microscopy, including HRTEM, EDX, and EELS to quantitively describe structural and chemical evolution of the titanium oxidation process upon heating. Spectroscopy measurements show that Ti oxidation undergoes a two-step process: at 300 °C, Ti is first oxidized into TiO and further oxidized into crystalline TiO$_2$ at 500 °C, and no more Ti is detected as being oxidized in TiO completely. At a similar initiation temperature, the Ti-based sample supports more oxygen transport, thus a greater number of elementary exothermic reactions, causing greater heat per unit volume. In turn, this drives the system into the self-sustaining reaction mode where sufficient energy is present to activate mass transport across the continuously forming terminal oxide until the reaction is completed. This study confirms that Ti can be of great interest in the addition or replacing Al in nanothermites, for applications where it is desirable to lower the ignition temperature.

References: