CENTRE
D'ÉLABORATION
DE MATÉRIAUX
ET D'ÉTUDES
STRUCTURALES

HIGHLIGHTS 2023

cnrs

CENTRE D'ÉLABORATION DE MATÉRIAUX ET D'ÉTUDES STRUCTURALES

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SUMMARY

EDITO

We are delighted to present the 2023 edition of the CEMES highlights.

You'll find our best results, published in top-tier international journals. You will see that our work continues to be based on theoretical and experimental studies, and on original instrumentation that enables us to achieve ultra-high resolutions, not only spatially but also spectrally and temporally.

Noteworthy among these significant happenings in CEMES is undoubtedly the important activity surrounding the development of molecules, materials and devices by physical means (sputtering, ion implantation), by chemical synthesis or in our clean room, which are subsequently investigated in our laboratory. Thus, the first 'E' in the CEMES acronym is gaining ever greater prominence.

In this collection, you will see the successes achieved in our joint laboratory with HITACHI. Our team was able to obtain the first pulsed electron beam and the first cathodoluminescence spectrum on the HITACHI 3300 microscope. These results mark the completion of our prototype transfer on a commercial microscope to successfully conclude the first joint laboratory HC-IUMI1. As a result of all this work, a second joint lab, called HC-IUMI2, has been launched and will be officially inaugurated in early 2024. The objective now is to demonstrate the power of this tool for physics in general, and more specifically, in the science of matter.

You will also see that the laboratory has acquired new equipment that will allow us to keep up with international state-of-the-art: a camera with direct electron detection for operando electron holography experiments, and a high-contrast microscope for in situ experiments and the observation of defects, particularly in metallurgy. For these advances, we thank CNRS (CNRS Physics institute and the «Occitanie Ouest» regional delegation), the Occitanie region, Toulouse-city council, and the French state. Thanks to these supports and also to the success of laboratory members to various project proposals, this year has also enabled us to acquire and renew laboratory equipment, which are more standard but essential for our day-to-day activities.

Finally, you will see that year 2023 has been rich in communication and scientific outreach events. Our open days in October, labeled in the framework of the year of physics, have met with great success. With the COVID years now behind us, we were able to gather for a laboratory seminar, this time in the village of Carla Bayle in Ariège. The photo on the right page aptly describes the remarkable spirit of cooperation and bonhomie that presided over these two days.

With great regret, we note the demise of an active member of CEMES, Olivier Auriol, who passed away way before his time and after enduring great suffering. Our thoughts are with him.

In 2024, we will begin to write self-assessment reports and our project for the coming years, which will allow to globally evaluate the activities of the laboratory. We hope that this effort, despite being somewhat tedious, will generate an enthusiastic and constructive reflection on the laboratory and its future.

We hope you enjoy reading the significant happenings in CEMES in the year 2023 and we wish you a successful and prosperous year 2024.

Alain Couret
Director, CEMES

Bénédicte Warot-Fonrose
Associate director
CEMES

Muriel Rougalle
Secretary General
CEMES

EDITO

Nous sommes très heureux de vous présenter l'édition 2023 des faits marquants du CEMES.

Vous y trouverez nos plus beaux résultats, publiés dans des revues du meilleur niveau international. Vous verrez que nos travaux continuent à s'appuyer sur des études théoriques et expérimentales et sur une instrumentation originale qui nous permet d'atteindre des résolutions ultimes, spatiales bien sûr, mais aussi temporelles et spectrales. Un fait marquant des faits marquants est sans nul doute l'activité de plus en plus importante autour de l'élaboration par voies physiques (bâtis, implanteurs), par synthèses chimiques ou en salle blanche des molécules, matériaux et dispositifs, que nous étudions ensuite au laboratoire. Le premier E de l'acronyme CEMES prend de plus en plus d'ampleur.

Vous verrez dans ce recueil les succès acquis dans le cadre du laboratoire commun avec HITACHI. Notre équipe a obtenu le premier faisceau d'électrons pulsé et le premier spectre de cathodo-luminescence sur le microscope HITACHI 3300. Ces résultats marquent la fin du transfert du prototype sur ce microscope commercial et clôturent avec succès le premier laboratoire commun HC-IUMI1. Grâce à tout ce travail, un second laboratoire commun HC-IUMI2 est lancé et sera inauguré officiellement au début 2024. L'objectif est maintenant de montrer la puissance de cet outil en physique en général et plus spécialement en science de la matière.

Vous verrez aussi que le laboratoire a reçu de nouveaux équipements qui lui permettront de se maintenir à l'état de l'art international, une caméra à détection directe des électrons pour l'observation operando par holographie électronique des champs locaux et un microscope haut contraste pour les expériences in situ et l'observation des défauts, en particulier pour la métallurgie. Que le CNRS (CNRS-Physique et la Délégation Régionale d'Occitanie Ouest), la Région Occitanie, Toulouse-Métropole et l'Etat soient remerciés. Grâce à ces soutiens et aussi à des succès sur des appels à projets des membres du laboratoire, cette année nous a permis également d'acquérir et de renouveler des équipements de laboratoire, plus standards mais indispensables pour accompagner nos activités au quotidien.

Vous verrez enfin que cette année 2023 a été riche en évènements de communication et de médiation scientifique. Nos journées portes-ouvertes d'octobre, labellisées dans le cadre de l'année de la physique, ont encore connu un grand succès. Les années COVID derrière nous, nous nous sommes retrouvés pour un séminaire du laboratoire délocalisé dans le village ariègeois du Carla Bayle. La photo ci-dessus illustre bien le remarquable esprit qui a présidé à ces deux journées.

Très malheureusement, le laboratoire a perdu un de ses membres en activité, Olivier Auriol, bien trop jeune et après bien trop de souffrances. Nous pensons à lui.

En 2024 commencera le processus d'évaluation du laboratoire par la rédaction de notre rapport d'autoévaluation et la finalisation de notre projet pour les prochaines années. Nous souhaitons que ce processus, certes parfois fastidieux, génère une réflexion enthousiaste et constructive sur le laboratoire et son avenir.

Nous vous souhaitons une bonne lecture de ces Faits Marquants 2023 du CEMES, et une très belle et riche année 2024.

Alain Couret
Directeur du CEMES

Bénédicte Warot-Fonrose
Directrice Adjointe du CEMES

Muriel Rougalle
Secrétaire Générale du CEMES

EXPERIMENTALLY-VERIFIED ELECTROMECHANICAL MODELING OF QUANTUM DOTS

THE ENGINEERING AND MODELING OF CHARGE CARRIERS' LOCALIZATION IN EPITAXIAL QDS

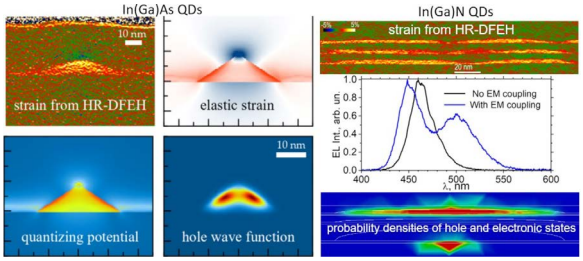
Researchers from CEMES, Ioffe Institute and UNICUSANO developed experimentally-verified models for optical emission of epitaxial In(Ga)As and In(Ga)N quantum dots. The models considered In-Ga intermixing, QD reshaping and generation of 3D strain fields. Specific hole wave function at the ground state was determined in In(Ga)As QDs. Novel emission properties were achieved and explained in a multilayer structure with electromechanically coupled In(Ga)N QDs.

Three-dimensional (3D) confinement of charge carriers within epitaxial In(Ga)As and In(Ga)N quantum dots (QDs) allows to considerably improve efficiency of light-emitting diodes and lasers. The engineering of the electron and hole localization in such QDs requires to consider In-Ga intermixing, QD reshaping and generation of 3D strain fields, which are intrinsic processes associated with QDs formation and burying in the bulk of the epitaxial film.

Researchers from CEMES, Ioffe Institute and UNICUSANO developed experimentally-verified models for optical emission of QDs in form of epitaxial In(Ga)As and In(Ga)N 3D islands embedded within GaAs and GaN matrices, respectively. The 3D composition distribution inside the nanometer-size QDs and their geometry were determined by solving the problem of solid mechanics of the stress-strain field inside and around QDs reconstructed from the 2D strain fields measured by dark-field holography in a high-resolution mode.

The parameters of the electron and hole ground states were evaluated in InGaAs QDs by solving the problem of the quantum mechanics within the same finite element model. The results of calculations appeared to be reasonably well consistent with experimentally recorded optical emission spectra. The model revealed a bagel-like shape of the hole wave function at the ground state, being beyond the predictions of simplified models, which should considerably impact the optical and magnetic properties of the QDs.

The 3D character of the strain field created around In(Ga)N islands was exploited to induce their vertical correlation in a multilayer structure. Such an approach allowed for QDs with novel optical properties providing a double wavelength emission in the blue and green spectral ranges. And this despite all layers had the same low In composition, which would have ensured blue emission only. With $\vec{k} \cdot \vec{p}$ calculations including electromechanical fields, the modeled optoelectronic properties of a multilayer structure evidenced some optimal In content arrangement in different layers which allowed for a significant reduction of the quantum-confined Stark effect, carrier tunneling through the QDs, an increase of wave functions overlap, and emergence of three distinct peaks in the spectral range, i.e. efficient QDs electromechanical coupling.



Two dimensional out-of-plane strain maps obtained by dark-field electron holography in high-resolution mode in In(Ga)As (on the left) and In(Ga)N (on the right) QDs used for 3D strain and composition fields reconstruction within finite element and $\vec{k} \cdot \vec{p}$ calculations and the modeled optoelectronic properties of such QDs.

A bagel-like shape of the hole wave function at the ground state of In(Ga)As QD is revealed. Normalized electroluminescence spectrum from the optimal multilayer structure of In(Ga)N QDs demonstrate double emission arising from electromechanically coupled QDs.

Experimentally-Verified Modeling of InGaAs Quantum Dots

A.N. Kosarev, V. V. Chaldyshev, and N. Cherkashin

Nanomaterials
12 (12), 1967 (2022)

Electromechanically Coupled III-N Quantum Dots

D. Barettin, A. V. Sakharov, A. F. Tsatsulnikov, A. E. Nikolaev, and N. Cherkashin

Nanomaterials
13(2), 241 (2023)

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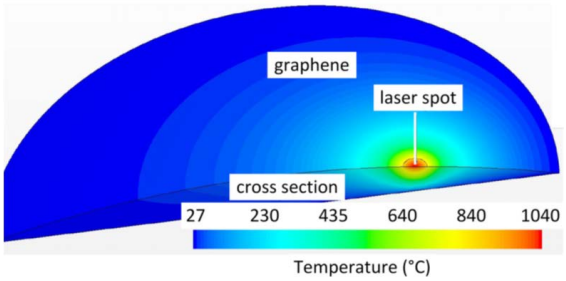
EXPLORING THE MECHANICAL PROPERTIES AND HEAT CONDUCTION OF GRAPHENE AT 1000°C

THE ELASTIC AND THERMAL PROPERTIES OF GRAPHENE WERE INVESTIGATED BY ILLUMINATING GRAPHENE BUBBLES WITH A LASER SPOT

The formation of standing optical waves lead to laser heating depending on the height of the graphene bubble, which results in Raman band oscillations when scanning the laser spot across the bubble. The profile of the bubble under laser illumination can be deduced from the Raman G band oscillations. A distinct swelling at the center of the bubble is observed which is attributed to the strong softening of graphene above 1000 °C.

Graphene has superior mechanical properties. Only a few theoretical studies are available on the elastic modulus of graphene up to 700 °C and there are no reported experimental studies so far on the elastic properties of graphene at elevated temperatures. We revisited the Raman spectral data of graphene bubbles since a closer examination of the Raman oscillations indicated smaller oscillations at the center of the bubble. Our spectral analysis shows a clear "swelling" at the center of the bubble where the temperature is highest, and the temperature at the edge of the swelling is found to be close to 1000 °C.

When considering heat transport through graphene only, analytical expressions for the temperature are derived. The so-determined temperature exceeds 2000 °C at the center of the bubble. When including heat conduction through the gas inside the bubble employing finite volume analysis, it is found that heat conduction through the gas in the bubble is significant and lowers the maximum temperature at the center of the bubble to below 1400 °C. The appearance of a swelling in large graphene bubbles when laser heated might eventually find application for creating a central hole in graphene membranes. This work is a collaboration between 2 laboratories in Toulouse (Laplace, CEMES) and a laboratory in South Korea (CMCM at UNIST).



Temperature distribution of graphene bubble when heated with a laser spot obtained by numerical finite volume analysis.

Probing elastic properties of graphene and heat conduction in graphene bubbles above 1000°C

W. Bacsa, F. Topin, M. Miscevic, J.M. Hill, Y. Huang, and R.S. Ruoff

Physical Review B
107, 195433 (2023)

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ABSOLUTE STRAIN AND RELATIVE DISPLACEMENT OVER HR-(S)TEM IMAGES

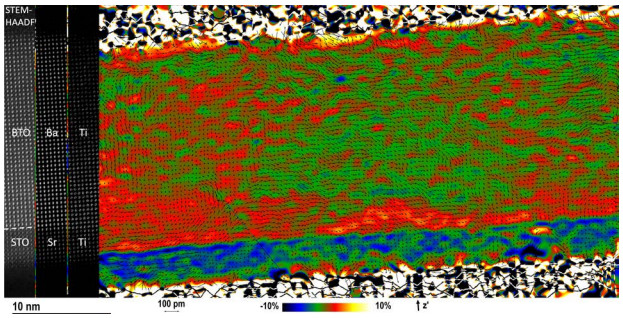
STRAIN AND RELATIVE DISPLACEMENT OF SUB-STRUCTURES OF COMPLEX CRYSTALS

Researchers from CEMES proposed two methods of reciprocal space treatment of HR-(S)TEM images, named AbStrain and Relative displacement. AbStrain allows for quantification and mapping of interplanar distances and angles, displacement fields and strain tensor components with reference to a user-defined Bravais lattice. Relative displacement provides atomic displacements between sub-structures, when a crystal is made up of two or more types of atoms.

For the reciprocal space treatment of HR-TEM and HR-STEM images like Geometric Phase Analysis (GPA), we overcame the limitation of using similar reference crystal structure in the same field of view, by directly treating the zone of interest corrected from the different types of image distortions specific to HR-TEM and HR-STEM imaging modes. We proposed to reconstruct the displacement fields and strain tensor components of the imaged structure with reference to a user-defined Bravais lattice by developing the method, named AbStrain, with two approaches. The first one provides the components of an absolute strain tensor and rigid body rotation by using the maps of measured reciprocal vectors and that of the Bravais lattice. Displacement field is then calculated by their integration. Alternatively, the second approach allows for the reconstruction of an absolute displacement field with reference to a Bravais lattice, from which strain and rotation are obtained by partial derivation. Interplanar distances and angles are reconstructed within both approaches from the absolute strain tensor and rigid body rotation maps.

We presented also the method, called Relative displacement, which allows for extracting images of sub-structures, when a crystal is made up of two or more types of atoms, and measuring atomic displacements with reference to each other, without the need to account for image distortions and be familiar with the crystal's structural characteristics. Such an approach is interesting to apply for complex semiconductors and functional oxides where polarization related displacement exists.

The two methods proposed here extend the range of possible crystalline materials that can be analyzed by the treatment of their HR-(S)TEM images. Examples include, but are not limited to, nanoparticles embedded within different types of matrices, free-standing nanowires, high-angle grain boundaries, multiple stacks of heterostructures of complex oxides and semiconductors and anti-phase domains.



Decomposition of cross-sectional HR-STEM-HAADF image of $BaTiO_3$ (BTO)-on-$SrTiO_3$ (STO) structure into images of sub-structures of Ba + Sr atoms and Ti atoms. Background: map of out-of-plane strain $\varepsilon_{zz'}^{BTO}$ of Ba+Sr sub-structure with reference to BTO Bravais lattice obtained by AbStrain. Arrows: relative displacement between the sub-structure of Ti atoms and the sub-structure of barycenters of Sr or Ba atoms obtained by Relative displacement

Quantitative mapping of strain and displacement fields over HR-TEM and HR-STEM images of crystals with reference to a virtual lattice

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Ultramicroscopy
253 (2023) 113778

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MORPHOLOGICAL SENSITIVITY OF SILVER NANOPARTICLES TO THE ENVIRONMENT

SILVER NANOPARTICLES STRUCTURAL EVOLUTION WITH TIME

Silver nanoparticles, major environmental pollutants, have been synthetized in vacuum, exposed to ambient air and investigated by atomic resolution imaging and *ab initio* calculations. Temperature, gaseous atmospheric pressure and surface contamination effects on nanoparticles morphology have been disentangled, paving the way to the understanding of nanoparticle ageing in environmental conditions at the atomic scale.

Metallic nanoparticles are widely used in industry, medicine and household goods and are of large interest for research activities in catalysis, optics, biosensing, cosmetics etc. Among them, silver nanoparticles (Ag NPs) have been developed intensively, especially due to their antimicrobial properties. Hence, they are a major source of environmental pollutants, with an evolutive toxicity level depending on their fate.

To date, very little is known about Ag NPs stability and structural evolution at the atomic scale, when exposed to environment. In the present studies, silver clusters have been synthetized in vacuum, exposed to ambient air and investigated by atomic resolution imaging (ac-STEM) to obtain isomer distribution statistics. Ag NPs exposed to air have been modelled by DFT and ab initio molecular dynamics (Ø = 1.66-1.80 nm). Temperature, gaseous atmospheric pressure and surface contaminant effects have been included in our simulations in order to determine Ag NPs thermodynamic stability and morphological changes, at short timescale (before ageing). Being able to untangle all these effects on the morphological changes of Ag NPs is a prerequisite to a rational design of efficient devices safer for environment.

Our key results show that Ag NPs exposed to air keep their metallic integrity all along the molecular dynamics simulations at room temperature. They are sensitive to the environment at various levels: (1) temperature determines the existence of a given morphology and structure; (2) shells of coadsorbed surface contaminants play a crucial role on the competition between Ag NPs morphologies; (3) nitrogen pressure exhibits a minority effect. Our theoretical results agree with the experimental statistics and paves the way to the understanding of nanoparticle ageing in environmental conditions at the atomic scale.

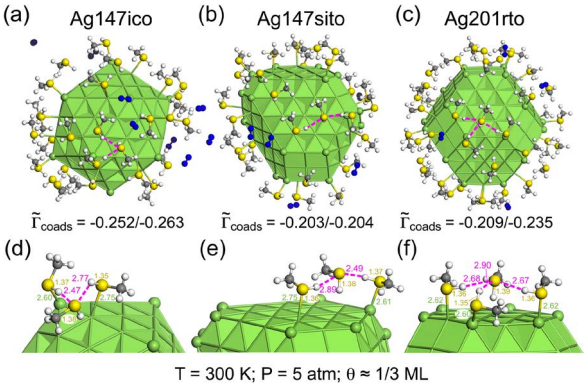

Illustration of final structures for contaminated Ag NPs immersed in gaseous nitrogen (5 atm), equilibrated at 300 K, extracted from AIMD trajectories and optimized in accurate conditions of (a) Ag147ico, (b) Ag147sito and (c) Ag201rto. In each case, an example of a coadsorption species composed of three or four methanethiol molecules is extracted from the optimized structures and depicted below them (d) Ag147ico (e) Ag147sito and (f) Ag201rto.

In such coadsorption species, two or three methanethiol molecules are bound through hydrogen bonds (see the dotted pink lines) to one contaminant which is adsorbed on the Ag NP via one Ag…H–SCH3 nonconventional hydrogen bond. Total coadsorption energies normalized to the nanoparticle surface area (in J m–2) are reported with ranges of values corresponding to the various coadsorption structures studied. Distances in figures (d)–(f) are given in Å. The color labels are green for Ag, yellow for S, blue for N, gray for C and white for H atoms. The color labels of distance values are defined as follows: green for Ag–S, yellow for S–H and pink for S…H.

Influence of Air Exposure on Structural Isomers of Silver Nanoparticles

J. Vernieres, N. Tarrat, S. Lethbridge, E. Watchorn-Rokutan, T. Slater, D. Loffreda, and R. E. Palmer

Communications Chemistry
6, 19 (2023)

Morphological Sensitivity of Silver Nanoparticles to Environment

N. Tarrat and D. Loffreda

Environmental Science: Nano
2023, 10, 1754

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DOUGHNUT-SHAPE LASER-CONTROLLED NANOSOURCES OF LIGHT

ANTENNAS FOR LIGTHT

Using lasers in singular polarisation states, it has been shown that it is possible to shape the emission of light in systems based on photon emitters coupled to silicon nano-antennas. This study provides a better understanding of light-matter interaction at these scales and opens the way to applications in the field of nanophotonics.

Nanophotonics (or nano-optics) is the study of the interaction of light with objects of dimensions much smaller than the wavelength, and one of its aims is to confine light to the nanometric scale in order to miniaturize optical components.

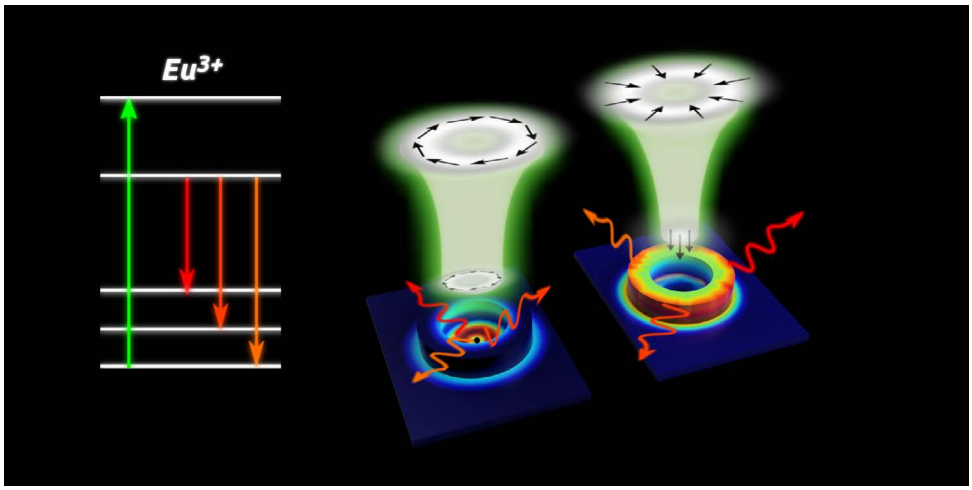
However, fabricating tiny light sources at this scale is a complex process, since photon emitters have to be positioned a few nanometers away around nanostructures acting as antennas. Their role, similar to that of a radio-frequency antenna, is to control and direct the emission of light.

This behavior is achieved by playing on the antenna's optical resonances when excited by a laser beam of appropriately chosen wavelength. These resonances generate local enhancements of the optical near-field, implying stronger light emission from photon emitters placed at these locations.

The NeO group, in collaboration with other French scientific teams, has demonstrated that it is possible to shape the optical near-field map around the nanostructure, using a doughnut-shaped laser beam and heterogeneous polarizations (azimuthal and radial).

The hybrid device developed for this study consists of a doped with rare-earth ions (Eu3+), deposited on silicon rings of different dimensions, acting as nano-antennas. The light emitted by this system was mapped to establish very precise maps of light amplification. These correspon exactly to the optical near-field «hot spots» obtained by numerical simulations.

These studies on hybrid systems, combining photon emitters and silicon nanostructures, open up interesting prospects for the production of nanoscale light sources. Such sources could be integrated into electronic components, as their manufacturing technologies are fully compatible with existing ones (CMOS technology).



Control of light emission of quantum emitters coupled to silicon nanoantenna using cylindrical vector beams

M. Montagnac, Y. Brûlé, A. Cuche, J.M. Poumirol, S.J. Weber, J. Müller, G. Larrieu, V. Larrey, F. Fournel, O. Boisron, B. Masenelli, G. Colas des Francs, G. Agez, and V. Paillard

Light: Science & Applications
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BORON-VACANCY SPIN DEFECT IN ISOTOPICALLY-PURIFIED HEXAGONAL BORON NITRIDE

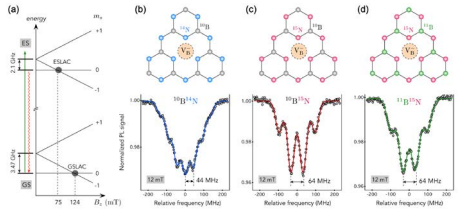
TOWARDS THE NEXT GENERATION OF QUANTUM SENSORS

The negatively-charged boron-vacancy (V_{B^-}) center in hexagonal boron nitride (hBN), created by ion implantation at Cemes, is promising for developing 2D spin-based quantum technologies. The electronic spin resonances of this point defect strongly depend on external perturbations (electric and magnetic fields, temperature) and can be controlled optically under ambient conditions even in the limit of atomic hBN layers, offering new prospects for quantum sensing with unprecedented proximity to the sample.

Quantum sensing technologies powered by solid-state spin defects have already shown a huge potential for covering the growing need for high-precision sensor. However, sensing methods based on spin defects in 3D materials, such as NV centers in diamond, are limited in spatial resolution due to the impossibility to engineer ultrathin and flexible sensors that could be as close as possible to the sample. Spin defects in atomically-thin 2D materials, like V_{B^-} centers in hBN, overcome these limitations.

To maximize the sensing performance of V_{B^-} centers, isotopically-purified hBN crystals were studied by Electron Spin Resonance (ESR) of V_{B^-} centers. Boron has two stable isotopes, ^{11}B (80% natural abundance (na)) and ^{10}B (20% na), while nitrogen occurs as either ^{14}N (99.6% na) or ^{15}N (0.4% na). In hBN crystals with natural isotopic content (h ^{11}B ^{14}N), when applying a weak static magnetic field Bz that splits the electron spin sublevels (Zeeman effect), the ESR of VB- centers is characterized by a complex seven-line structure resulting from the hyperfine interaction with the three ^{14}N nuclei placed in the first neighboring lattice sites. The hyperfine coupling with the second-neighbors boron atoms rather leads to an overall broadening of each ESR line. The other isotopic configurations of hBN (h ^{10}B ^{14}N, h ^{10}B ^{15}N, and h ^{11}B ^{15}N) were then studied in the same way.

This work shows that isotopic purification with ^{15}N yields a simplified and well-resolved hyperfine structure of V_{B^-} centers, while purification with ^{10}B leads to narrower ESR linewidths (see Figure). These results establish isotopically-purified h ^{10}B ^{15}N crystals as the optimal host material for future use of V_{B^-} spin defects in quantum technologies.



(a) Simplified energy level structure of the V_{B^-} center in hBN showing the electron spin sublevels ms = 0,±1 in the ground (GS) and excited states (ES), as well as their evolution with a static magnetic field B_z applied along the c-axis of hBN. Hyperfine structure of the V_{B^-} center in (b) h ^{10}B ^{14}N, (c) h ^{10}B ^{15}N, and (d) h ^{11}B ^{15}N crystals.

The next step now is to reduce the thickness of the hBN layer to achieve ultimate atomic-scale proximity between the sensor and the probed sample.
Cemes (*MEM team and ATP platform*) is involved in these promising developments by creating the VB- defects by ion implantation as an alternative technique to neutron irradiation, which main drawbacks are accessibility and potential hazard due to transmutation products. However, using ion implantation requires optimizing the ion/energy/dose combinations to create dense array of VB centers in ultrathin hBN flakes ideally down to the monolayer limit. This will be done by:
- Advanced Monte Carlo simulations to select implantation parameters that optimize V_B center formation.
- Performing wide range of ion implantations on exfoliated hBN flakes of various thicknesses.
- High-resolution transmission electron microscopy to measure V_B center density.

This work is supported by ANR QFoil (L2C, LPCNO, Cemes) and NanoX Q2D-Sens (LPCNO, Cemes)

Isotopic control of the boron-vacancy spin defect in hexagonal boron nitride

T. Clua-Provost, A. Durand, Z. Mu, T. Rastoin, J. Fraunié, E. Janzen, H. Schutte, J. H. Edgar, G. Seine, A. Claverie, X. Marie, C. Robert, B. Gil, G. Cassabois, and V. Jacques

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DISLOCATIONS OBSERVED IN 3D IN TIAL

THE SIMPLIFIED ELUCIDATION OF DEFORMATION MECHANISMS INSPIRES NEW ALLOY DESIGNS

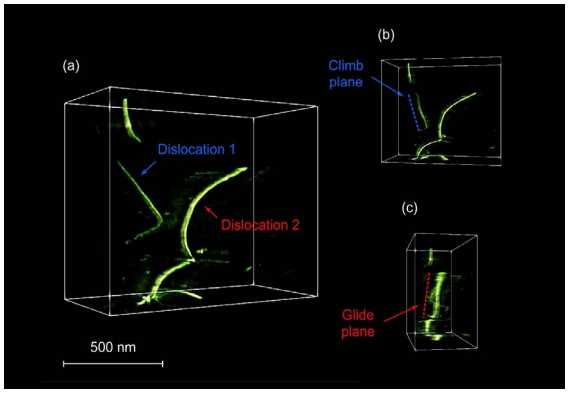
Elucidating the deformation mechanisms at the nanometric scale is often decisive in the design of new alloys. Controlling the deformation mechanisms at high temperature of the TiAl intermetallic would allow, for example, high-potential alloys for the aerospace industry to be developed. For this purpose, recent results from CEMES in Toulouse and CINaM in Marseille show that emerging approaches of electronic tomography are highly promising.

The deformation mechanisms at high temperature in metals, far from being fully understood to date, could be elucidated with greater ease thanks to three-dimensional reconstruction approaches. In the case of TiAl, this could be particularly attractive to inspire the design of new alloys, in the race to lighten hot parts in aircraft engines. The challenge would be to limit the movement of linear crystalline defects that control the undesirable deformation of the parts, namely dislocations.

To achieve this, it is necessary to determine whether the movement of the line of these defects takes place by successive jumps in the crystalline potential (glide), or by vacancy trapping (climb), in order to select the alloying elements that most effectively slow down these mechanisms. However, conventional transmission electron microscopy (TEM) methods are highly restrictive when it comes to identifying glide or climb, as the sample holders limit the observation of dislocations to a restricted angular range.

Electron tomography, by enabling 3D reconstruction of nanometric volumes and their 360° visualization, has spectacularly removed this obstacle. This technique first appeared in 2006 for the delicate observation of dislocations, and was subsequently taken up at the UMET of Lille by A. Mussi, but the teams at CEMES and CINaM have developed an original approach, enabling to go down to ultimate lateral resolutions (10 nm). To achieve such high-precision tomographic reconstructions, the key step was to align series of up to 100 images around a common tilt axis, with sub-pixel precision.

The idea was to adapt landmark recognition and tracking techniques, coming from the life sciences, to image alignment by successive iterations. This makes it possible to orientate dislocation displacement planes in space easily and with great precision, and thus to identify climb or glide mechanisms (cf. Figure). Thanks to this type of observation, it will be possible to select the alloying elements that slow down dislocations motion most effectively, such as tungsten and molybdenum for climb, or carbon and silicon for glide. 3D vision is therefore particularly promising for furthering the design of new alloys, by enabling much more systematic investigations.



Elucidation of deformation mechanisms in TiAl at 900°C, thanks to 360° 3D vision. (a) Volume of nanometric dimensions containing two dislocation loops. (b-c) Visualization of the volume from different angles, allowing to identify crystallographic planes of climb and glide for these two dislocations.

Habit planes of climbing and gliding dislocations in TiAl determined in three dimensions by electron tomography

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HOW DO YOU CREATE MOLECULAR "ORIGAMI" ?

SELF-ASSEMBLING STRUCTURES OF ARTIFICIAL PROTEINS

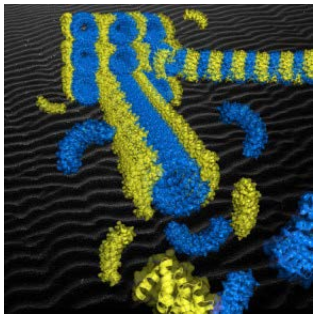
Four French teams are demonstrating the possibility of constructing ordered supramolecular architectures that form spontaneously from proteins specially designed for this aim. The key to this innovation is the engineering of highly regular proteins with repeated motifs and recognition surfaces that enable them to establish specific interactions.

While it is possible to build nanostructures of controlled shape by exploiting the double helix structure of DNA molecules (leading to assemblies commonly known as «DNA origami»), it remains much more difficult to build such precise structures from proteins. However, in living cells, highly sophisticated supramolecular architectures such as microtubules, actin filaments and flagella perform vital functions and are entirely made up of natural proteins. They assemble spontaneously because each protein has a particular shape that allows it to interact in a very specific way with other proteins, leading to complex architectures. Creating ordered supramolecular architectures of proteins would open the door to numerous applications in biology as well as in materials science.

In an interdisciplinary project involving biochemists and physical chemists from CEMES (CNRS), I2BC (CNRS / CEA / Université Paris Saclay), IPR (CNRS / Université de Rennes), CBI (CNRS / Université de Toulouse - Paul Sabatier) and ICB (CNRS / COMUE Université Bourgogne Franche-Comté), a generalisable method for constructing artificial protein architectures has been developed. Rather than modifying natural proteins, the scientists have chosen to design new proteins that are both highly regular and programmed to assemble in precise geometries capable of forming stable superstructures. One of these proteins, called a 'staple', has the role of precisely assembling several other proteins called 'bricks', their assembly naturally giving to the supramolecular three-dimensional architecture its structural complexity. The first challenge was to design and produce these proteins. Then, using a combination of techniques including X-ray scattering and cryo-electron microscopy, the researchers have shown that the proteins assemble in a few minutes, at room temperature and according to the planned architecture. This is an experimental first, the principle of which can be applied to other molecular systems.

This concept of protein origami promises architecture programming that is as efficient as DNA origami, but with the added potential for widespread use that comes with the extraordinary diversity of proteins in terms of chemical functions and molecular recognition. In particular, varying the spatial arrangement of the bricks and staples could make it possible to create a whole range of 'patterns' for organising nano-objects with respect to to each other (enzymes, nanoparticles, viruses, etc.), encapsulating active ingredients, guiding the growth of nanomaterials or structuring the interface between biological matter and a solid material. This initial experimental work therefore opens up major prospects, especially at a favourable time when computer tools for designing artificial proteins are becoming powerful and available.

Semi-experimental model of the origami of artificial proteins in which the superhelix of bricks (in blue) self-assembles by affinity with the staple (in yellow). The extreme regularity of the supramolecular structure obtained arranges the staples periodically along the superhelix and induces the formation of aligned origami crystals @ I2BC, CEMES, CBI, IPR and ICB



Design, synthesis, and characterization of protein origami based on self-assembly of a brick and staple artificial protein pair

L. Moreaud, S. Viollet, A. Urvoas, M. Valerio-Lepiniec, A. Mesneau, I. Li de la Sierra-Gallay , J. Miller, M. Ouldali, C. Marcelot, S. Balor, V. Soldan, C. Meriadec, F. Artzner , E. Dujardin, and P. Minard

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EXTENSION OF ON-SURFACE SYNTHESIS: FROM 2D TO 3D

TOWARDS HETEROMOLECULAR COVALENT MULTILAYERS

2D surface synthesis makes it possible to couple molecules on monocrystalline surfaces to form new molecules or oligomers that are often unattainable by chemistry. This approach was limited to two-dimensional systems in direct contact with the substrate. It was attractive to explore the third dimension to create molecular multilayer systems with complete control over the organization of intermolecular bonds.

In this experiment, the first molecular layer is formed of 3,5-bis(carboxylic acid)-phenyl-3-maleimide (BCPM). This molecule has both a phenyldicarboxylic function designed to promote its self-assembly on the substrate, in this case an Au gold surface (111), and a maleimide ring whose activated double bond can be involved in cycloaddition reactions with one or two other carbon-carbon double bonds. The second molecule used here is a fullerene C60, as it owns a large number of potentially reactive double bonds over its entire surface.

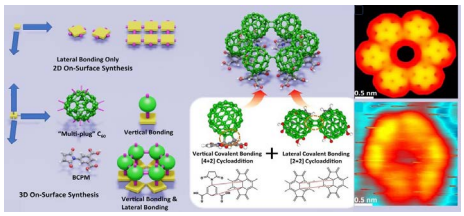

Figure 1. Schematic diagram of 3D synthesis-on-surface. On right, the STM images of the obtained "six-petal flowers" of covalently coupled C60 (bottom : experimental, top: calculated image) bonded on the top of six self-assembled BCPM

The synthesis takes place on a Au(111) gold surface in an ultra-high vacuum chamber and the evolution of the reaction is monitored by scanning tunneling microscopy (STM). The first step is the sublimation of BCPM, which self-organizes into 6-petal flowers with a central cavity . The fullerene C60 is then sublimated on this monolayer, first filling the cavities, then forming a monolayer with a physisorbed C60 above each BCPM. The temperature is then raised to 370K for 30 min, which induces a [4+2] cycloaddition reaction between the BCPM and the C60 onto which it is adsorbed. Then a new annaealing at 490K for 30 min allows the formation of 2 [2+2] bonds between each C60 and its two neighbors.

This structure appears as six-petal flowers, made of covalently bonded fullerenes. Here we were able to form a bi-layer heteromolecular system with complete control of covalent bonds in all three dimensions. Further extension to multilayers will give access to a wide variety of new molecular materials and devices.

Extending on-surface synthesis from 2D to 3D by cycloaddition with C60

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POLYCRISTALLINE CORE@SHELL NANOPARTICLE, A 3D NANO-PUZZLE

ASSOCIATING IRON, GOLD AND SILVER, IT IS A MATTER OF SYMMETRY

Associating iron, gold and silver under ultrahigh vacuum can lead to the self-assembly of a polycrystalline AuAg alloy shell, growing epitaxially on a single-crystal iron core in the shape of a truncated rhombohedral (or rhombic) dodecahedron. The 18 shell grains have to fit together, and around the core, in a nano-puzzle-like organization, of which there are in theory 186 different solutions, distributed in 13 point groups of symmetry.

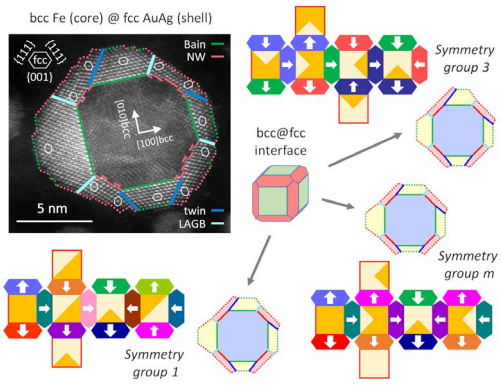
Associating iron (bcc structure) with noble metals (fcc structure) can lead to the formation of nanoparticles with a core@shell chemical order, thanks to the conjunction of a miscibility gap, the difference in surface energy, and the existence of two epitaxial relationships.

We thus achieved Fe@AuAg nanoparticles in a Mantis ultrahigh vacuum chamber by iron deposition followed by gold and silver deposition, and we studied their structures with the support of the Centre de Microcaractérisation Castaing. We observed that the iron core can be in the shape of a truncated rhombic dodecahedron covered by a polycrystalline AuAg alloy shell. This shell presents as many nano-grains as the core has faces, namely 18, distributed in 6 grains in coherent epitaxial relationship (so-called Bain) with the iron, and 12 grains in semi-coherent epitaxial relationship (so-called Nishiyama-Wasserman) with the iron. The grains of the two types are joined by an equal number of twins and low-angle grain boundaries (LAGB).

Understanding, predicting and classifying the possible morphologies of these nanoparticles is akin to solving a 3D nanometric puzzle, the pieces of which are the nano-grains and the core. The pieces have to fit together allowing the accommodation of the crystalline lattices, not only between the grains and the core, but also between the grains themselves.

A symmetry analysis shows that there exist, in theory, 186 possible solutions to this puzzle, distributed in 13 point groups of symmetry, all of lower order that the core symmetry (highest cubic symmetry). Symmetry reduction originates from the Nishiyama-Wasserman (NW) epitaxial relationships, at each of the 12 concerned interfaces.

A major consequence is that a population of these nanoparticles will present a variability of morphology and symmetry. If the symmetry breaking is randomly distributed at each NW interface, 80% of the nanoparticles will be asymmetric. Extending this approach to other core shapes also succeeds in predicting dissymmetrical or dramatically off-centered morphologies experimentally observed in Fe@Au nanoparticles with more irregularly shaped cores.



Analysis of a Fe@AuAg nanoparticle observed in section, and three possible reconstructions of its morphology, belonging to groups 3, m or 1, the only ones compatible with the experimental observation. The patterns are developments of the interface in the shape of a truncated rhombic dodecahedron. The symmetry breakings are symbolized by the white arrows and the same color for the hexagons means that there are symmetrical to each other. The yellow shades symbolize the resulting morphology of the shell grains.

Morphology and symmetry driven by lattice accommodation in polycrystalline bcc-fcc core-shell metallic nanoparticles

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NEW EQUIPMENT FOR TRANSMISSION ELECTRON MICROSCOPY

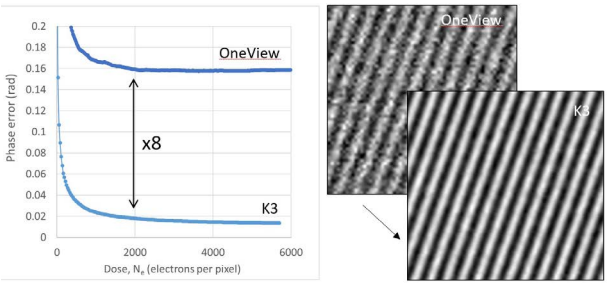
A NEW MICROSCOPE, NEW CAMERA, NEW X-RAY SPECTROMETER, AND A NEW SAMPLE PREPARATION SYSTEM: 2023 HAS PROVEN TO BE A SUCCESSFUL YEAR FOR THE RENEWAL OF OUR TRANSMISSION ELECTRON MICROSCOPY (TEM) EQUIPMENT.

New Transmission Electron Microscope

Our recently acquired JEOL JEM-2100Plus TEM (image on the right) funded by the CPER Occit'EM will seamlessly facilitate ongoing in-situ experiments, typically straining and/or heating. This is made possible by adapting the column both to custom made sample holders fabricated in CEMES and the forthcoming Force-Control-Straining holder. The TEM is equipped with two cameras, one with high speed for video applications and the other with exceptional resolution that is particularly well suited for tomography studies. It also includes motorized diaphragms and a computer environment to enable future Python interfacing and automation.

Installation of a Direct Electron Detector (K3, Gatan) on the I2TEM Microscope

Compared with the previous CMOS Detector (OneView, Gatan), there is a spectacular improvement in the signal-to-noise ratio of electron holograms acquired on the I2TEM microscope (image below). Electric and magnetic fields in devices and nanostructures can be measured with greater precision and at higher spatial resolution. The electron dose can also be reduced by an order of magnitude, allowing the study of beam-sensitive materials. This new camera was acquired thanks to the FEDER Occit'EM.



New X-ray photon analysis spectrometer

The Tecnaï F20 microscope now has a new X-ray photon analysis spectrometer installed—the EDAX EDS Elite T. This spectrometer can detect X-ray photons from light elements (B, C, N, and O) more effectively owing to its larger detection surface and the absence of a window upstream of the detector. In conjunction with another spectrometer to analyze electron energy losses (GIF Tridiem from Gatan), this set up enables the detection of a wide range of chemical compounds with a single microscope.

Installation of a latest generation of ion polishing system

The new low-energy ion polishing PIPS II system developed by Gatan featuring weakly accelerated argon ion beams allows samples for transmission electron microscopy to be prepared while minimizing artefacts induced by ion etching. This purchase was made in the framework of the Horizon Europe «AddMorePower» project coordinated by the Fraunhofer Institute in Dresden (IKTS) and Infineon (KA-I, Villach).

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COMMUNICATION AND DISSEMINATION OF SCIENCE

In terms of communication and dissemination of science, 2023 will have been marked by the launch of our new website, which is designed to be more attractive, modern and easy to read. A new feature of the site is a virtual tour of the clean room.

In terms of internal communication, we should mention the creation of the newsletter *Les Infos du Lundi*, which is published every two weeks to summarize all the upcoming meetings for the fortnight and introduce newcomers. We should also mention, and the editorial refers to it, the internal seminar organised over two days in Ariège.

On the secondary education front, the laboratory is continuing its collaboration with *Club Cemes* at Berthelot secondary school, the *Déclics* operation and the national *Apprentis chercheurs* initiative, one of the final presentations of which was organised at Cemes in June.

Also in June, Toulouse's first *Festival de Caves* found the laboratory basement an ideal venue for two of the 28 performances staged in these unexpected locations: at Cemes, in association with the *Maison de quartier*, this pocket theatre format found its audience.

In the autumn, as part of the *Fête de la science* and the *Année de la physique*, almost 400 people visited Cemes to find out more about the research being carried out there. On that Saturday, more than 40 people from the laboratory were involved in welcoming visitors, based on discovery tours organised around 12 workshops, including one in the clean room and one for children.

The previous day, two classes of first-year students from the region had come to discover the laboratory. A week earlier, a new *Curieuse Visite Curieuse* had sold out with the concept of discovering original places in Toulouse via dramatised tours. It was in our case an opportunity to evoke the epic of optics, from photons to electrons, and to take the spectators to the Boule of course, but also to the HC-IUMI microscope (see pages 18-19).

The year ended with the highly original occupation of part of our premises by the film crew for season 2 of the Toutouyoutou series: some forty people, four days of filming, and a unique opportunity for all people from Cemes to see the making of a film up close.

1% by and with Louise Guillame-Bert ©Compagnie Vorace

Filming of the Toutouyoutou series

Visit to the clean room during the open days

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ULTRAFAST ELECTRON MICROSCOPY AT CEMES: A NEW JOINT LABORATORY BETWEEN CNRS AND HITACHI HIGH-TECHNOLOGIES

Developments around ultrafast electron microscopy at CEMES have seen significant progress over the last year. The promising results obtained on a first prototype of ultrafast Transmission Electron Microscope (UTEM) developed in CEMES motivated the creation in 2018 of a first joint laboratory between CNRS and the Japanese company Hitachi High-Technologies. The objective of this laboratory called HC-IUMI (Hitachi-CNRS Infrastructure for Ultrafast Microscopy) was to transfer the ultrafast electron source from the old HF2000 microscope which served as the basis for the prototype to an HF3300, a last generation 300 kV Hitachi TEM. The installation of this microscope in a completely renovated room in 2019 was followed by several important modifications of the instrument to prepare the transfer of the ultrafast electron source. The transfer of the ultrafast electron source started in January 2022 (see figure 1). This step, by far the most difficult, involved touching the critical parts of the microscope, those which impose the most drastic conditions on vacuum and high voltage. In June, after more than half a year of struggle the first laser-driven electron emission has been obtained on the new UTEM. This achievement successfully closed the 5 years of the first joint laboratory.

Given the success of the first joint laboratory, CNRS and HHT decided in 2023 to continue the scientific and technological cooperation in the form of a new joint laboratory. This second joint laboratory aims at going beyond proof-of-principle experiments and demonstrate the full potential of the ultrafast CFEG-technology on several cutting-edge applications in nano-optics, nano-mechanics, and nanomagnetism. The initial assets of the ultrafast CFEG technology developed in CEMES: femtosecond/nanometer spatio-temporal resolution, unique beam spatial coherence are not only maintained on the new HC-IUMI UTEM but also completed by several other unique features.

Figure 1: Pictures of the gun transfer from femtoTEM to HC-IUMI. Top: removal of the ultrafast gun assembly from FemtoTEM. Bottom: Installation in HC-IUMI by S. Meuret and H. Lourenço-Martins.

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Probably the most important one is the possibility, also available on the CEMES I2TEM to have the sample in two different positions: one above and one in the objective lens, known as the Lorentz and high-resolution stages. The CEMES mechanical department designed and built two light injectors especially for this microscope. The first now installed in the Lorentz stage is a flat mirror that allows us to inject light onto the sample with a spot size of 100 to 10 µm. The second is a parabolic mirror with micrometer precision position control in x, y, and z. This mirror allows us to collect light efficiently or focus it on a 2 µm spot. This so-called "double-stage" feature expands significantly the potential of the HC-IUMI UTEM for coherent control experiments.

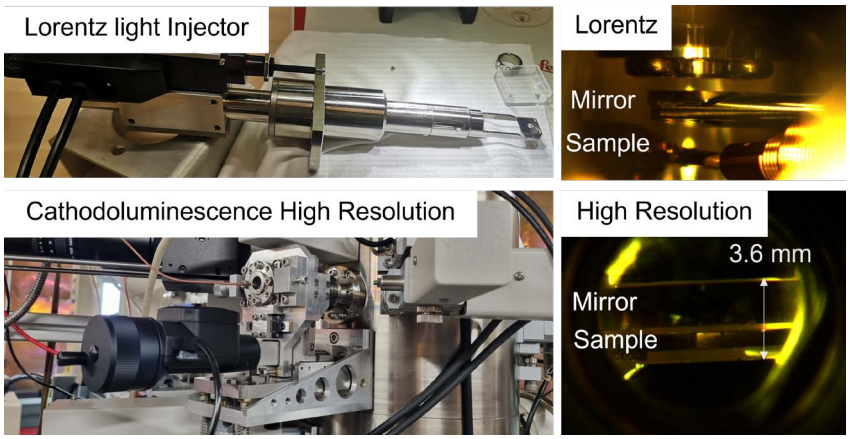

Figure 2: The two light injectors designed and built by the mechanical department. Top: the Lorentz injector with the flat mirror, left outside the column and right a view of the mirror and the sample in the microscope chamber. Bottom: High resolution injector with the system attached to the column (left) and the visualization of the HR chamber with a pole piece gap of 3.6 mm (right).

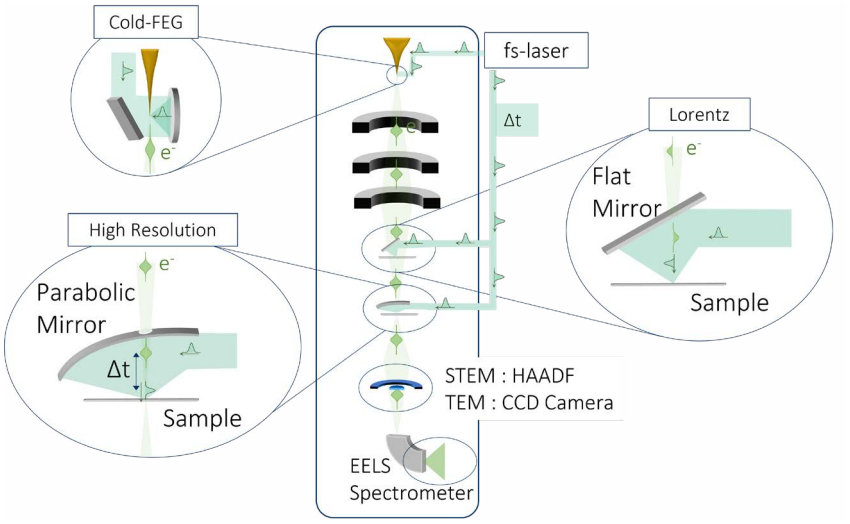

Figure 3: Sketch of the HC-IUMI microscope with the laser driven cold-field emission gun and the two samples position (Lorentz and high resolution).

The instrumental developments reported above are realized by a young team which has benefited from the recent recruitment of four PhD students. For the time being, the four students are using the two main electron-based spectroscopies available on the UTEM: PINEM and TRCL. PINEM (Photon Induced Near-field Microscopy) analyzes the energy lost and gained by electrons interacting with the near-field induced by a laser. It can be used either to study the optical near-field around nanostructures or to tailor the electron beam by making it interact with a spatially shaped laser beam. TRCL (time-resolved cathodoluminescence) is a powerful technique that analyzes the light emitted by the sample (cathodoluminescence) to track the charge carrier relaxation in a semiconductor nanostructure after an electron excitation.

Despite this year's accomplishments additional work and a few more months are still needed before the PINEM and TRCL experiments can be performed routinely on the new HC-IUMI instrument. On a longer term, the unique femtosecond cold-field emission gun, will make HC-IUMI the ideal UTEM for performing time-resolved diffraction and electron holography experiments. We hope to be able to develop these unique features in the near future!

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