CENTRE D'ÉLABORATION DE MATÉRIAUX ET D'ÉTUDES STRUCTURALES

HIGHLIGHTS 2024

**CENTRE D'ÉLABORATION DE MATÉRIAUX
ET D'ÉTUDES STRUCTURALES**

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SUMMARY

4 Edito

6 Towards all electrical skyrmion detection in van der Waals tunnel junctions

7 Mapping electrical resistivity in phase change memories by electron holography

8 New TEM holders for in situ dynamic studies

9 Elastic interactions can increase (and not decrease!) the velocity of dislocations

10 X-ray diffraction of sp^2 carbons: innovation with well-established techniques

11 How do gold and silver organize inside a nanoparticle?

12 An interdisciplinary approach to the design of nano-antimicrobials

13 Origin of brittleness in TiAl alloys

14 Vortex-like polarization in $BaTiO_3$ nanoislands epitaxial on silicon

15 Imaging optical fields at the attosecond and nanometer scales

16 Nano-fabrication in the CEMES cleanroom

17 Sébastien Weber, 2024 Laureate of the CNRS Crystal Medal

18 The CEMES Commits to Reducing Greenhouse Gas Emissions

EDITO

Nous sommes très heureux de vous présenter l'édition 2024 des faits marquants du CEMES.

Comme chaque année, vous y trouverez de beaux résultats scientifiques dans les domaines d'expertise du laboratoire, physique de la matière condensée, la chimie moléculaire, les nanosciences et la science des matériaux. Vous verrez que les modélisations et développements théoriques occupent de plus en plus de place dans nos travaux, dans des études autonomes, ou combinés aux travaux expérimentaux. Plusieurs faits marquants illustrent une autre spécificité forte du laboratoire qui est d'étudier la dynamique de phénomènes physiques, sous sollicitation lumineuse, mécanique, électrique ou magnétique, à des résolutions spatiales, spectrales ou temporelle ultimes. Enfin, ces faits marquants confirment que développements instrumentaux et méthodologies originales sont souvent au cœur de nos études.

Vous trouverez également dans ce recueil deux articles sur des actions à long terme du laboratoire. Depuis plusieurs années, nous travaillons à la structuration de nos activités d'élaboration par voie physique de nano-matériaux, -objets et -dispositifs, avec la mise en place de moyens techniques et humains à la hauteur de nos ambitions. Vous lirez que nous sommes maintenant en capacité d'élaborer des objets d'études originaux, premières pierres de bon nombre de nos projets de recherche. Par ailleurs, depuis quelques années nous travaillons à évaluer l'empreinte environnementale de notre recherche et à la diminuer. Vous verrez que nous avons calculé nos émissions de gaz à effet de serre et en avons déterminé les origines principales. Nous commençons à prendre des premières mesures pour les réduire.

Cette année le CEMES a pu recruter une ingénieure de recherche et un chargé de recherche. Justine Harmel a été lauréate d'un poste qui l'amènera à piloter nos activités en salle blanche. Valentin Magné renforcera notre activité en synthèse de molécules sur surface dans le groupe GNS. Nul doute que tous deux donneront un élan supplémentaire à ces activités. C'est l'occasion pour nous de remercier le CNRS pour son soutien. Nous avons eu également la satisfaction de voir Sébastien Weber, Ingénieur de Recherche, obtenir la médaille de cristal du CNRS pour ses travaux en instrumentation dans le domaine de l'optique et pour tout son travail autour de son logiciel libre PyMoDAQ, qui permet le pilotage des manips et le traitement des données acquises. De beaux succès personnels de nos collègues qui en accompagnent des collectifs.

Le laboratoire a eu l'immense douleur de perdre une des membres, Mme Chantal Brouca-Cabarrecq, maîtresse de conférences à l'université et chercheuse au CEMES. Nous pensons à elle.

L'année 2025 sera celle de l'évaluation HCERES et du renouvellement de l'équipe de direction. Forts de nos beaux résultats, de nos belles réalisations techniques, de nos succès individuels et collectifs, nous aborderons cette échéance dans la sérénité et avec le but de construire l'avenir. Le changement de direction sera un marqueur du passage de témoin d'une génération à une autre. Laboratoire de recherche, le CEMES se doit d'être en perpétuelle évolution face aux défis scientifiques et sociétaux qui se présentent à lui et nul doute qu'il sera à la hauteur des enjeux.

Nous vous souhaitons une bonne lecture de ces Faits Marquants 2024 du CEMES, et une très belle et riche année 2025.

Alain Couret
Directeur du CEMES

Bénédicte Warot-Fonrose
Directrice Adjointe du CEMES

Muriel Rougalle
Secrétaire Générale du CEMES

EDITO

We are very pleased to present the 2024 edition of the CEMES Highlights.

As every year, you will find remarkable scientific results in the laboratory's areas of expertise: physic of condensed matter, molecular chemistry, nanosciences, and materials science. You will see that modeling and theoretical developments are playing an increasingly important role in our work, either in standalone studies or in combination with experimental work. Several highlights illustrate another key strength of the laboratory: studying the dynamics of physical phenomena under light, mechanical, electrical, or magnetic stimuli, at ultimate spatial, spectral, or temporal resolutions. Finally, these highlights confirm that instrumental developments and original methodologies are often central to our studies.

In this collection, you will also find two articles on the laboratory's long-term activities. For several years, we have been structuring our activities in the physical fabrication of nanomaterials, -objects, and -devices, with the implementation of technical and human resources aligned with our ambitions. You will read that we are now capable of producing original objects of study, serving as foundational elements for many of our research projects. Furthermore, in recent years, we have been working to assess and reduce the environmental footprint of our research. You will see that we have calculated our greenhouse gas emissions and identified their main sources. We have begun to take initial measures to reduce them.

This year, CEMES succeeded in recruiting a research engineer and a researcher. Justine Harmel was selected for a position that will lead her to manage our cleanroom activities. Valentin Magné will strengthen our activities in surface molecular synthesis within the GNS group. There is no doubt that both will give new momentum to these activities. This is an opportunity for us to thank the CNRS for its support. We also had the satisfaction of seeing Sébastien Weber, Research Engineer, awarded the CNRS Crystal Medal for his work in instrumentation in the field of optics and for his contributions to the development of PyMoDAQ, his open-source software for experiment control and data processing. These are significant personal successes for our colleagues, which complement collective achievements.

The laboratory is deeply saddened by the loss of one of its members, Mrs. Chantal Brouca-Cabarrecq, Associate Professor at the university and researcher at CEMES. She is in our thoughts.

The year 2025 will bring the HCERES evaluation and the renewal of the management team. With our excellent results, technical achievements, and individual and collective successes, we approach this milestone with confidence and the aim of shaping the future. The leadership transition will mark the passing of the baton from one generation to the next. As a research laboratory, CEMES must constantly evolve to address the scientific and societal challenges it faces, and there is no doubt that it will rise to meet these challenges.

We wish you an enjoyable read of these 2024 Highlights of CEMES and a very happy and prosperous 2025.

Alain Couret
Director of CEMES

Bénédicte Warot-Fonrose
Deputy Director of CEMES

Muriel Rougalle
General Secretary of CEMES

TOWARDS ALL ELECTRICAL SKYRMION DETECTION IN VAN DER WAALS TUNNEL JUNCTIONS

STUDY OF NONCOLLINEAR MAGNETORESISTANCE BY AB INITIO QUANTUM TRANSPORT

Magnetic skyrmions – topologically stabilized chiral spin structures with size down to the nanometer scale – have emerged as a promising avenue to realize next-generation spintronic devices. A researcher from the MEM group at CEMES-CNRS, in collaboration with the University of Kiel (Germany), has just proposed a novel approach to detect skyrmions using an electric current.

Ten years ago, Albert Fert and co-workers first proposed to use skyrmions in a racetrack memory in their seminal paper. Today, many other potential applications of skyrmions are being explored, ranging from logic devices to neuromorphic or quantum computing. An essential prerequisite for most applications is reliable electrical detection of individual skyrmions or other topological spin structures.

In 2020, magnetic skyrmions were first experimentally observed in two-dimensional (2D) van der Waals (vdW) magnets, providing an ideal playground to advance skyrmion technology towards the single-layer limit with large tunability via external stimuli.

Scientists from CEMES-CNRS and the University of Kiel in Germany have now been able to demonstrate that all-electrical detection of skyrmions in tunnel junctions based on 2D vdW magnets (see Fig. 1a) is feasible with straightforward implementation into device architectures. They report on their discovery in the journal *Nano Letters* [1].

They proposed a tunnel junction based on the vdW $Fe3GeTe_2$/germanene interface, where sub-10 nm skyrmions can be stabilized even without magnetic fields, as demonstrated by their previous publication[2]. An extremely large noncollinear magnetoresistance (NCMR) of above 10,000% is predicted for atomic-scale skyrmions a vdW tunnel junction based on graphite/$Fe3GeTe_2$/germanene/graphite. Notably, the NCMR is more than two orders of magnitude higher than that obtained for conventional transition-metal interfaces.

From a fundamental point of view, the physical mechanism is explained by the interplay between the spin mixing and orbital symmetry matching effects at the interface. Additionally, their work also highlights the crucial importance of using the nonequilibrium Green's function (NEGF) approach for quantum transport on noncollinear spin structures in tunnel junction devices, going beyond the Tersoff-Hamann (TH) approximation (see Fig. 1b). Their proposal opens a new route to realize skyrmion racetrack memories based on atomically thin vdW materials with full-electrical writing and reading, using a low-energy-consuming method.

[1] **Proposal for all-electrical skyrmion detection in van der Waals tunnel junctions**

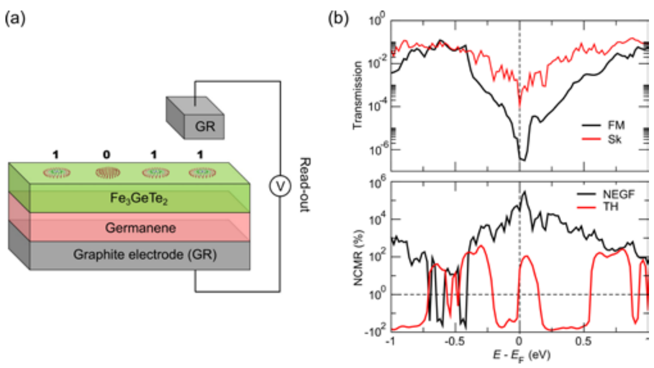
D. Li, S.Haldar, and S. Heinze

Nano Lett.
24, 2496–2502 (2024)

[2] **Strain-driven zero-field near-10 nm skyrmions in two-dimensional van der Waals heterostructures**

D.Li, S. Haldar, and S. Heinze

Nano Lett.
22, 7706–7713 (2022)



(a) Schematic representation of the proposed vertical tunnel junctions with nonmagnetic electrodes for electrical readout of skyrmions in 2D vdW magnets, e.g., in racetrack memory.

(b) Transmission functions for the ferromagnetic state (black) and the Néel-type skyrmion state (red). Corresponding NCMR (black), calculated by the nonequilibrium Green's function (NEGF) method. The NCMR obtained in the Tersoff-Hamann (TH) approximation (red) is shown for comparison.

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MAPPING ELECTRICAL RESISTIVITY IN PHASE CHANGE MEMORIES BY ELECTRON HOLOGRAPHY

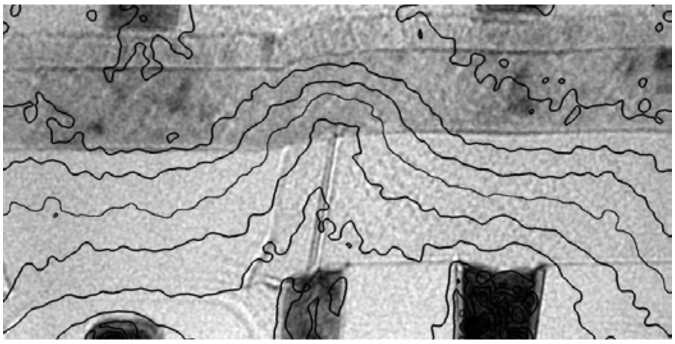
STUDYING THE ACTIVE AREA OF AN INDIVIDUAL DEVICE IN OPERATION

A new method based on *operando* electron holography was developed to map the resistivity at the nanoscale across the active area of a working individual device. This method has been applied on a phase change memory cell in wall architecture and directly highlighted unexpected features. On switching the memory state by electrical pulses inside the TEM, we studied the resulting electric field and demonstrated that electrical resistance is inhomogeneous near the heater.

The use of electrical resistivity as a parameter to drive devices is receiving increasing attention due to the development of memristors, resistive random-access memory (RRAM) and phase-change memories (PCM). Applications range from active components for more energy-efficient machine learning and in-memory computing to emerging photonic applications. Additionally, PCM promise better performance and a strong interest for low-energy applications.

Phase-change materials such as GST materials exhibit a huge change of electrical resistivity between the amorphous (high resistance) and crystalline phase (low resistance). To read the device, the resistance is measured by biasing the top and bottom electrode connected to a thin metallic filament called the “heater”. To write, a high-amplitude current pulse is injected, whose exact form depends on whether the operation is to stabilize the crystalline phase (SET) or the amorphous state (RESET). Current passing through the heater and GST layer causes localised Joule heating; the associated rise in temperature in turn causes the phase change. To SET, a relatively long pulse allows gradual crystallisation of the amorphous state whilst for RESET, a short pulse induces rapid melt-quench of the crystalline to amorphous state. Once the current pulse has passed, no power is required to maintain the state.

In order to understand the operation of devices, different *in situ* techniques have been developed to monitor the phase transition, notably in transmission electron microscopy (TEM). A distinction needs to be made between *in situ* experiments that heat the whole specimen, usually thin films, to provoke the phase change and *operando* experiments that aim to be closer to the actual operation of devices by injecting current pulses *in situ*. However, all depend on structural or chemical analysis and do not probe directly the local electrical properties. Here we present a method based on *operando* electron holography to determine the local resistance with nanometre spatial resolution. We demonstrate the technique on a working industrial PCM device and reveal the inhomogeneity of the resistivity in the active layer. Beyond the interest for PCM, the technique is applicable to many other devices where changes in local electrical resistance are of primary importance.



Measuring electrical resistivity at the nanoscale in phase change materials

L. Zhang, F. Lorut, K. Gruel, M.J. Hÿtch, and C. Gatel

Nano Lett.
24, 5913–5919 (2024)

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NEW TEM HOLDERS FOR IN SITU DYNAMIC STUDIES

DEVELOPMENT OF TEM SUPPORTS FOR INJECTING RADIO-FREQUENCY SIGNALS

In collaboration with CISTEME and A3D Design, CEMES has developed and produced two new object holders for the *in situ* injection of high-frequency electrical signals. The measurements carried out show that a bandwidth of several GHz is now accessible. These novel instruments for MET will enable dynamic studies of electrically excited systems with sub-nanosecond time resolution.

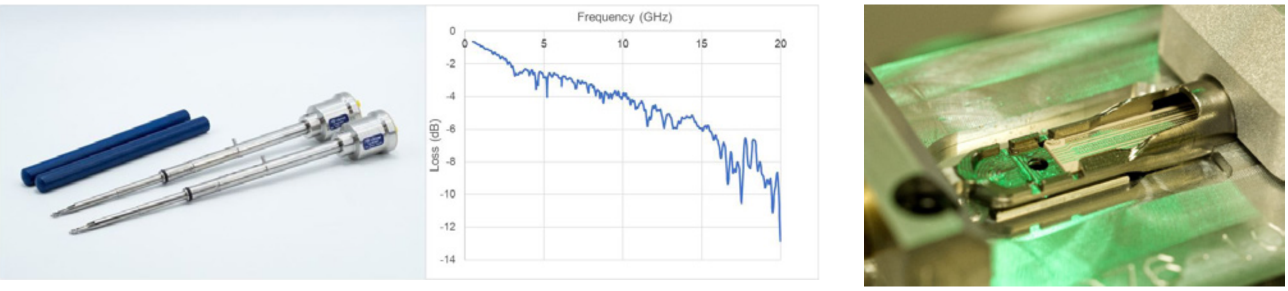
For several years, CEMES laboratory has been developing in situ studies of nanosystems using transmission electron microscopy (TEM) . Part of this work aims at performing electron holography experiments in order to quantitatively map the electric and magnetic fields of electrically excited nanosystems and nanodevices with a sub-nanometric resolution.

However, the results obtained to date are based on static studies and do not allow access to dynamic processes. In particular, CEMES has long been seeking to develop a new method for imaging radiofrequency (RF) electromagnetic waves in magnetic nanomaterials (spin waves) using TEM. One of the challenges is to inject signals of several GHz in situ or pulsed signals of less than 1 ns through dedicated object carriers to the nanostructure, or to nearby antennas. The limited bandwidth of commercially available sample holders greatly reduces the injected power and considerably increases the width of the electrical pulses.

In collaboration with CISTEME (a company specialising in the study of RF signals) and A3D Design (a company specialising in precision mechanical engineering), two CEMES researchers and members of the department of mechanics have designed and manufactured two sample holders, one with 2 RF lines and the other with 4, each with a bandwidth of 5 GHz with less than 3 dB loss and up to 18 GHz with less than 10 dB loss over the whole frequency range.

Compatible with the I2TEM microscope dedicated to electron interferometry and in situ experiments, and the HC-IUMi microscope currently under development for time-resolved studies, these new TEM holders will soon make it possible to study spin waves and many other dynamic phenomena in situ, such as the trapping of charges during the charge/discharge cycles of a nanocapacitor or the mapping of magnetic vortex precession trajectories.

This unique development was funded under the EUR NanoX (SWIME), ANR PRC (EHIS 21-CE42-003) and PEPR SPIN (Spin Charac) projects. A patent application is currently under consideration.



Radiofrequency TEM holders and measurement of loos in dB as a function of the frequency

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ELASTIC INTERACTIONS CAN INCREASE (AND NOT DECREASE!) THE VELOCITY OF DISLOCATIONS

HOW IN SITU STRAINING EXPERIMENTS CAN CONTRIBUTE TO REFINE DDD CALCULATIONS

Heavy plastic deformation hardens materials through a process described by the Taylor law, which assumes an average internal stress. In our study, using in situ transmission electron microscopy we found that the law fails at low temperatures. Our results show that dislocation motion is driven by localized peak stresses, and cooperative motion between screw dislocations can lead to unexpectedly high velocities and negative hardening.

Metals and other crystalline materials are considerably hardened by heavy plastic deformation. This "cold-working" process results from the intense multiplication of dislocations which are mutually blocked as a result of their elastic interactions. Hardening is often described by an average "internal stress" increasing with plastic deformation (Taylor law). This rough description has been recently improved by the discrete dislocation dynamics (DDD) method which involves the computation of all individual interactions and subsequent evolution of the whole substructure under stress.

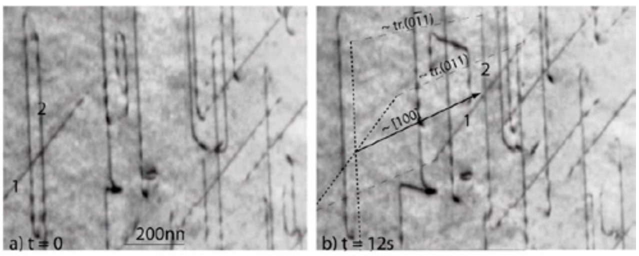
In our work based on in situ straining experiments in a transmission electron microscope that allow one to directly observe the motion of dislocation under stress between 95K and 1500K, we have shown that even such complex calculations are not sufficient in metals with a body-centered-cubic (BCC) structure like iron and ferritic steels strained at low temperature.

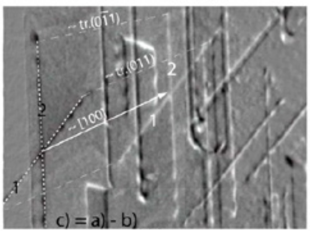
We have indeed studied all possible dislocation interactions in BCC iron at various temperatures, and the results show that the concept of average internal stress is unsuitable to describe real situations. For instance, the velocity of a screw dislocation is not determined by its average driving stress, but by the highest local stress along its whole line. Interacting screw dislocations of different types can also move cooperatively at a high velocity up to ten times their individual uncoupled velocities (figure), leading to a strongly negative hardening effect, resulting from tangential components of interaction stresses not taken into account before. Such unexpected behaviors will be used to improve future DDD calculations.

Elastic interactions between screw dislocations in iron

D. Caillard

Modelling Simul. Mater. Sci. Eng.
32 (2024) 035027





Dislocations moving under stress in iron at 110K. The two pictures (a) and (b) are separated by 12s. The difference-image (c)=(a)-(b) shows that the cross formed by the two coupled dislocations 1 and 2 has moved over a much larger distance (arrowed) than all other individual dislocations.

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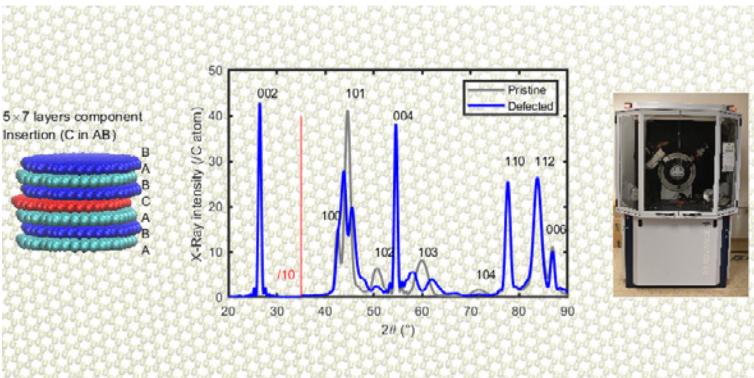
X-RAY DIFFRACTION OF sp^2 CARBONS: INNOVATION WITH WELL-ESTABLISHED TECHNIQUES

GO FASTER AND FURTHER IN ANALYSIS WITH A GLOBAL "BOTTOM-UP" APPROACH

Switching from CPU to GPU and, in the future, to AI, will enable to describe more accurately the description of X-ray diffraction peaks of lamellar carbon compounds ranging from turbostratic carbon to graphite. Where discrepancies existed, and where some signatures were misunderstood, the «bottom-up» approach completed by the generation of fitting functions explains the smallest details of diffractograms, based on interference effects.

For several years now, CEMES has been developing a new approach based on a bottom-up approach combined with adjustment functions first managed by CPU and then GPU to analyse the diffractograms of graphitisable carbons, which are lamellar materials with the particularity of being distributed along a structural continuum. The diffractograms have signature shapes that are not taken into account by conventional analysis softwares, including subtle interference effects due to the complexity of the stacking sequences in the elementary crystallite. We have identified the specific component of the crystallites responsible for these misunderstood signatures for intermediate crystallisation states: pairs of AB-stacked graphenes separated from the other components by rotational disorders, which strongly modify the *10(0)* and *11(0)* zones of the diffractograms. Taking them into account resolves all the discrepancies unexplained over the last 80 years, and gives a coherent set of characteristics derived from an analysis based on parameterised functions. For carbons closer to graphite, it is stacking faults that are responsible for the deviations from standard (and unrealistic) models[1], but analysing their influence on the whole diffractograms is now an impossible task without the use of AI.

The latest development in the saga that began in research 10 years ago and started being published 5 years ago[2] involved looking at disordered carbons to elucidate a small-angle peak that had remained unexplained to this day[3]. The tools developed can easily be applied to all diffractograms, as we are now doing on a routine basis ([4] and forthcoming articles). Thanks to the GPU, it is already possible to get away from the relative but deceptive comfort of empiricism! The impact on the community is significant. An important step has been taken: the method is now sufficiently validated for the tools developed to be made available to anyone (*https://github.com/PascalPuech/X_Ray*). The completion of the full analysis of experimental diffractograms of all types of carbon will come over the long term from artificial intelligence, which will be based on a gigantic database of calculated diffractograms.



[1] **Addressing the effect of stacking faults in X-ray diffractograms of graphite through atom-scale simulations**
P. Puech, M. Jeanningros, D. Neumeyer, and M. Monthioux
Carbon Trends
13 (2023) 100311

[2] **New insight on carbonisation and graphitisation mechanisms as obtained from a bottom-up analytical approach of X-ray diffraction patterns**
P. Puech, A. Dabrowska, N. Ratel-Ramond, G. Vignoles, and M. Monthioux
Carbon
147 (2019) 602-611

[3] **Specific X-Ray, Raman and TEM signatures of cellulose-derived carbons**
P. K. Mubari, T. Beguerie, M. Monthioux., E. Weiss-Hortala, A. Nzihou, and P. Puech
'C'
8 (2022) 4

[4] **Analysing the modifications of carbon black and other fillers after pyrolysis of model tyres**
P.K. Mubari, E. Weiss-Hortala, M. Monthioux, S. Moyano, A. Bowles, G. Fowler, L. Moulin, and P. Puech
Sustainable Materials and Technologies
40 (2024) e00904

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HOW DO GOLD AND SILVER ORGANIZE INSIDE A NANOPARTICLE?

CONTRIBUTIONS OF A COMBINED EXPERIMENTAL/MODELING APPROACH

Although nano-alloys are of great scientific and practical interest, their formation remains poorly understood. In this study, we explore the gold-silver system by combining experiments and simulations to elucidate formation mechanisms at the atomic scale. We synthesized nanoparticles by gas-phase aggregation and performed machine-learning-assisted simulations to further our understanding of the crystallization process. Our results reveal gold segregation on the surface of nanoparticles, which we discovered to be caused by charge transfer and electrostatic interactions, challenging previous ideas.

Although nanoalloys are of great scientific and practical interest, the processes leading to their formation are not yet well understood. Key characteristics of the alloys, such as crystal phase, chemical arrangement, and morphology, are challenging to control at the nanoscale, complicating their industrial application. In this study, we focus on the gold-silver system, two of the most common noble metals, and combine experiments and simulations to uncover how these alloys form at the atomic level.

We synthesized nanoparticles using an advanced gas-phase aggregation technique and analyzed their morphology and chemical distribution at the atomic scale using transmission electron microscopy. We employed machine-learning-assisted molecular dynamics simulations to model the crystallization process, transitioning from liquid droplets to nanocrystals.

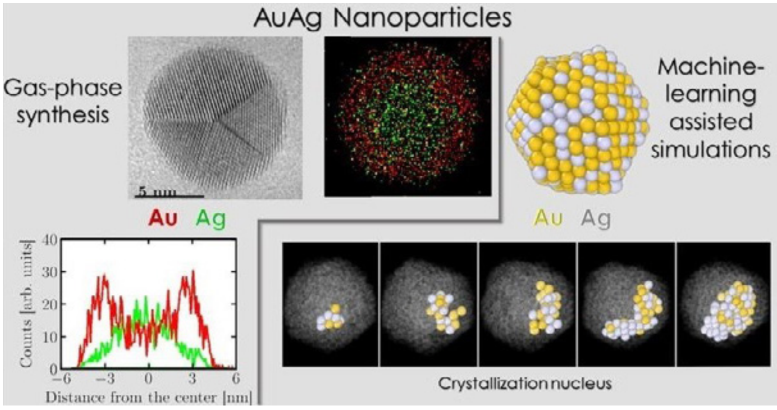
Our study reveals that, as for the monometallic nanoparticles, the majority of the formed nanoparticles exhibit a unique fivefold symmetric shape, such as icosahedra and decahedra. However, we found that gold atoms, rather than silver atoms, concentrate at the surface of the nanoparticles, regardless of the alloy composition. This segregation tendency contrasts with previous studies and influences both the crystallization dynamics and the resulting crystal arrangement. This observation challenges previous notions and could alter our understanding of the formation mechanisms of these nanoparticles.

Finally, we demonstrated that this surprising segregation dynamics is driven by charge transfer and electrostatic interactions, rather than surface energy considerations as previously thought. The use of machine learning was essential for modeling the crystallization process, allowing us to analyze the obtained data more effectively.

Exploring the formation of gold/silver nanoalloys with gas-phase synthesis and machine-learning assisted simulations

Q. Gromoff, P. Benzo, W. A. Saidi, C. M. Andolina, M. J. Casanove, T.Hungria, S. Barre, M. Benoit, and J. Lam

Nanoscale
2024,16, 384-393



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AN INTERDISCIPLINARY APPROACH TO THE DESIGN OF NANO-ANTIMICROBIALS

BENEFITS OF COUPLING PHYSICS TO ROBOTICS, QUANTUM CHEMISTRY & MATHEMATICS

By adapting and combining robotics-inspired structural exploration algorithms, energy potentials from quantum chemistry and mathematical tools to assess the (dis)similarity between two complex hybrid nano-systems, we are gaining understanding of their structural and electronic properties, paving the way for the rational design of nano-antimicrobials, highly promising objects for combating resistant microorganisms.

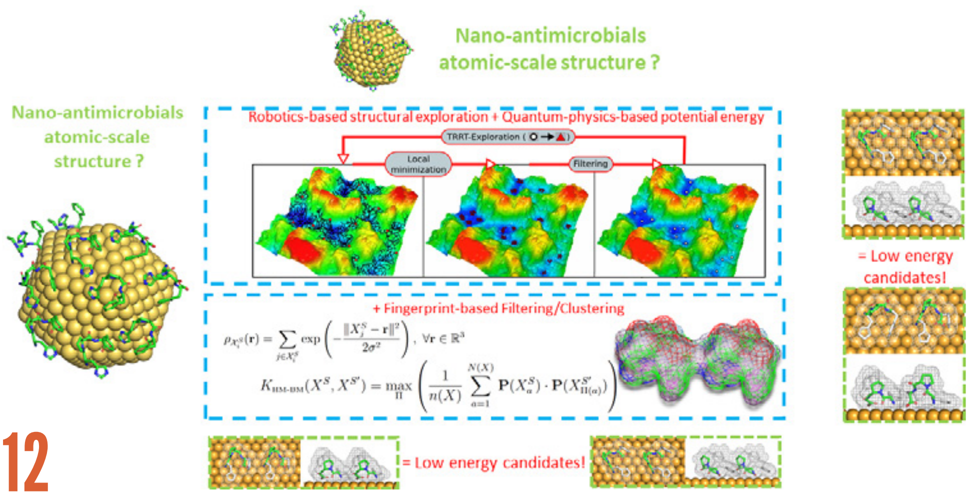
The development of nano-antimicrobials (metal nanoparticles functionalized with bioactive molecules) is a promising strategy in the international fight against resistant microorganisms. However, their atomic and electronic structures are poorly understood, which is a major obstacle to their rational design.

In order to achieve a structural understanding of functionalized surfaces, and to be able to apprehend the electronic mechanisms at play, we have adapted/optimized methods to explore their conformations in an efficient and non-redundant way, and interfaced it with a quantum chemistry code. The robotics-inspired algorithm, named IGLOO (Iterative Global Exploration and Local Optimization), uses tree-based exploration and dynamically adjusts its exploration strategy to scan the energy landscape evenly and focus on promising regions, avoiding redundant exploration. The interfaced quantum chemistry code, deMonNano, enables the energy calculations required for IGLOO exploration to be performed with a DFTB quantum energy potential.

Within such structural explorations, a major challenge is to assess the (dis)similarity of the nano-systems explored to obtain a clustering of the latter. Since the nano-antimicrobials we model have the particularity of being homomolecular (i.e. containing a large number of a given molecule), we have adapted a fingerprint-based method called SOAP (Smooth Overlap of Atomic Positions), taking advantage of the structural architecture of homomolecular systems to minimize irrelevant comparisons of atomic environments. This has enabled us to reduce computational costs and noise in (dis)similarity measurements, with the consequence of producing more meaningful clustering results than native methods, by better capturing key structural differences between states.

Our next steps will be to carry out the developments needed to perform these explorations not only on flat surfaces, but also on nanoparticles functionalized by a large number of ligands.

This work is being carried out as part of a collaboration between LAAS, LCPQ, IMT, MPI-Stuttgart and CEMES.



Exploring molecular energy landscapes by coupling DFTB potential with a tree-based stochastic algorithm: Investigation of the conformational diversity of Phthalates

V. Milia, N. Tarrat, C. Zanon, J. Cortés, and M. Rapacioli

Journal of Chemical Information and Modelling
64 (2024) 3290

Dependence of lactose adsorption on the exposed crystal facets of metals: a comparative study of gold, silver and copper

N. Tarrat, J. C. Schön, and J. Cortés

Physical Chemistry Chemical Physics
26 (2024) 21134

IGLOO: an Iterative Global exploration and LOcal Optimization algorithm to find diverse low-energy conformations of flexible molecules

W. Margerit, A. Charpentier, C. Maugis-Rabusseau, J. C. Schön, N. Tarrat, and J. Cortés

Algorithms
16 (2023) 476

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ORIGIN OF BRITTLENESS IN TiAl ALLOYS

HOW A COMBINATION OF MICROSCOPY TECHNIQUES SOLVES AN OLD METALLURGICAL QUESTION

One of the solutions for drastically reducing the environmental impact of aero-engines is to introduce TiAl alloys into the stages of turbojet engines operating at over 800°C, due to the low density of these materials. The looked-for resistance to these high temperatures can be achieved by introducing heavy elements that will lead to the formation of a β_o phase with an ordered, centered cubic structure. The TNM alloy belongs to this class of strong alloys, but suffers from very low ductility, making it impossible to industrialize.

As part of an international ANR project, CEMES researchers worked with their Austrian colleagues, the inventors of this TNM alloy, to understand the reasons for its premature fracture during a deformation cycle. To detect the origin of this effect, it was necessary to combine several techniques of electron microscopy, taking them to extremes.

View (a) shows that the ω_o phase contains a second phase which appears in the form of diffuse nanoprecipitates. The low contrast results from the small difference in chemical composition between these two phases. These results, combined with zone-axis diffraction patterns (b) and high-resolution images (c), showed that these precipitates took on a ωo structure and were needle-shaped with characteristic dimensions of the order of a few nanometres.

In-situ deformation experiments, a technique that enables the deformation mechanisms to be observed directly under stress, showed that although they represent a hardening obstacle to deformation (d), these precipitates can be crossed by dislocations and are therefore not directly responsible for the failure of the alloy. On the other hand, as shown in view (e), dislocations will form pile-ups of hundreds of dislocations to cross the precipitates, thereby creating stress concentrations that will ultimately lead to material failure.

These nanoprecipitates are therefore indirectly responsible for the premature failure of the material.

Plasticity and brittleness of the ordered βo phase in a TNM-TiAl alloy

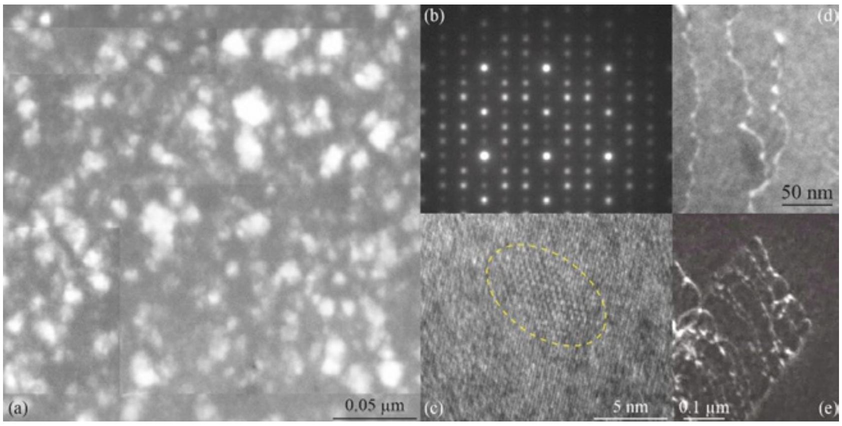
Molénat G., Galy B., Musi M., Monchoux J.P., Toualbi L., Clemens H, Thomas M., and Couret A.

Intermetallics
151, 18, 2022

ω precipitation and its influence on the deformation mechanisms of a TNM Ti-Al alloy

Molénat G., Monchoux J.P., Warot-Fonrose B., and Couret A.

Materials Characterisation
218 (2024) 114509



Analysis of the structure and characteristics of nano-precipitates of ωo phase in the TNM alloy. (a) dark-field image, (b) diffraction pattern in zone-axis, (c) atomic resolution image of a nanoprecipitate, (d) dislocations anchored on nanoprecipitates, moving during an in situ deformation experiment and (e) head of a dislocation pile-up.

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VORTEX-LIKE POLARIZATION IN $BaTiO_3$ NANOISLANDS EPITAXIAL ON SILICON

2D POLARIZATION MAP FROM HRSTEM IMAGES TREATED WITH ABSTRAIN/RELATIVE DISPLACEMENT

Two researchers from the MEM group have demonstrated the formation of trapezoidal funnel-shaped nano-islands in thin films of the ferroelectric oxide $BaTiO_3$ epitaxial on silicon. They revealed their singular, downward-convergent polar state, which can be seen as a swirling vortex of polarization flux and can be reversibly electrically switched, a promising result for future topological nanoelectronics applications.

A fascinating aspect of nanoscale ferroelectric materials is the emergence of topological polar textures, which include various complex and stable polarization configurations. The manipulation of such topological textures through external stimuli like electric fields holds promise for advanced nanoelectronics applications but integration of polar texture on silicon, the ubiquitous electronic technology platform, remains challenging.

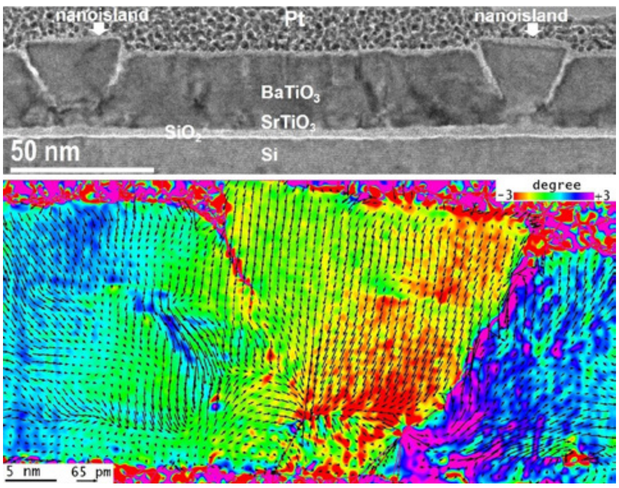
In the context of the ANR FEAT project, our colleagues from the Helmholtz-Zentrum für Materialien und Energie group in Berlin succeeded to grow epitaxial $BaTiO_3$ films on Si using a $SrTiO_3$ template modifying the classical passivation step of the Si surface by introducing an excess of Sr in order to disrupt the Sr (2×1) surface with Sr aggregates.

High angle annular dark field (HAADF) high resolution STEM images of these films revealed the presence of trapezoidal nanoislands in place of these Sr-enriched zones. By correcting these images for distortions using the "AbStrain" method, the rotation of unit cells within the nano-islands was highlighted (colored mapping). At the same time, the direction of displacement of Ti atoms relative to the position of the Ba(Sr) cell barycentre, linked to polarization, was obtained after isolating Sr/Ba and Ti atoms using the "Relative displacement" approach (arrows superimposed on the coloured mapping). The particular "down-convergent" polarization configuration was thus identified.

Complementary investigations by piezoresponse force microscopy (PFM) demonstrated that such center down-convergent polarization domains can be reversibly switched by an electric field to center up-divergent domains. PFM data reconstruction and phase field modelling gave also insight into the 3D patterns of the polarization confirming the presence of a whirling component of the polarization around the nanoisland axis, which confers chirality.

The ability to create and electrically manipulate chiral whirling polar textures in $BaTiO_3$ nanostructures grown monolithically on silicon holds promise for applications in future topological nanoelectronics.

Cross-sectional (110)Si STEM image with two nanoislands in a $BaTiO_3$ film and colored map of the unit cells rotation where superimposed arrows indicate the direction/intensity of the polarization



Switchable topological polar states in epitaxial $BaTiO_3$ nanoislands on silicon

I. Olaniyan, I. Tikhonov, V. Hevelke, S. Wiesner, L. Zhang, A. Razumnaya, N. Cherkashin, S. Schamm-Chardon, I. Lukyanchuk, D.-J. Kim, and C. Dubourdieu

Nature Communications
15 (2024) 10047

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

N. Cherkashin, A. Louiset, A. Chmielewski, D.J. Kim, C. Dubourdieu, and S. Schamm-Chardon

Ultramicroscopy
253 (2023) 113778

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IMAGING OPTICAL FIELDS AT THE ATTOSECOND AND NANOMETER SCALES

PHASE-LOCKED INTERACTIONS ENHANCE THE TIME RESOLUTION OF ELECTRON MICROSCOPES

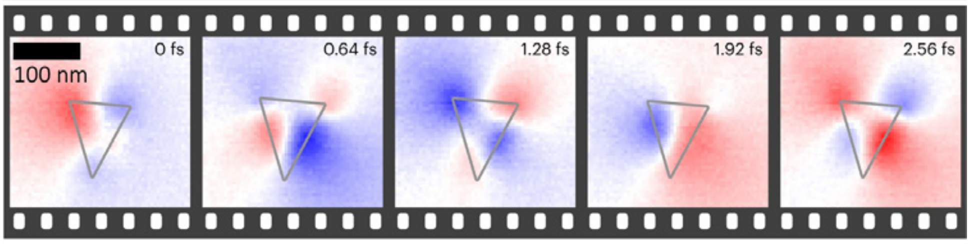
In a series of works, we have developed different techniques harnessing phase-locking in electron-laser interaction to push ultrafast transmission electron microscopes' resolution - so far limited to 10-13s - to the attosecond regime (10-18s). These five orders of magnitude improvement enables the recording of attosecond movies showing the oscillation of nano-optical excitations (e.g. surface plasmon polaritons) at the nanometer scale (see figure).

Observing and manipulating the dynamics of nano-optical excitations requires imaging techniques combining sub-wavelength spatial resolution and sub-cycle temporal resolution. In that aim, the last decade has seen the development of ultrafast transmission electron microscopy (UTEM) which combines the temporal resolution of ultrashort laser sources (few hundreds of femtoseconds) with the spatial resolution of electron microscopes (sub-nanometer) in a pump-probe scheme: a first laser pulse (pump) excites the sample, which is then probed by a pulsed electron beam (probe). This technique has been able to resolve a plethora of phenomena but remains too slow for nano-optical excitations which generally oscillate with a period of few attoseconds.

In this series of works, we have developed different techniques able to push the resolution of UTEM to the attosecond regime.

All of them are based on the same idea: sequential phase-locked interactions. Indeed, while in a conventional UTEM the electron beam measures a laser-driven sample, here we have added a second interaction stage with a fixed laser field to imprint a reference phase on the electron beam. This pre-modulation leads to interferences in the electron-sample interaction, thus revealing the sub-cycle temporal dynamics of the target. Our works explore different variations of this technique in which the reference interaction can occur either with another sample, a different optical excitation within the same sample or different scattering orders.

All these techniques have been experimentally demonstrated on the UTEM of the Göttingen university. For example, one can observe the oscillations of a localized surface plasmon mode in a gold nano-triangle on the figure above. The colormap represents the plasmonic electric field (negative values in blue, positive values in red).



Attosecond electron microscopy by free-electron homodyne detection

J. H. Gaida, H. Lourenço-Martins, M. Sivis, T. Rittmann, A. Feist, F. J. García de Abajo, and C. Ropers

Nature Photonics
18, 509-515 (2024)

Lorentz microscopy of optical fields

J. H. Gaida, H. Lourenço-Martins, S. V. Yalunin, A. Feist, M. Sivis, T. Hohage, F. J. García de Abajo, and C. Ropers

Nature Communications
14, 6545 (2023)

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NANO-FABRICATION IN THE CEMES CLEANROOM

The CEMES cleanroom offers tools and instruments dedicated to micro- and nano-fabrication. The highly adaptable local platform aims to design and fabricate original objects that are the first building blocks of some laboratory's scientific projects. The range of objects goes from model ones conceived for research projects within the laboratory to prototypes of nano-devices with applicative purposes. It also includes systems designed for the implementation of advanced measurement techniques (TEM, optical spectroscopy, near-field microscopies). Since its commissioning in 2013, the cleanroom has gradually developed in terms of equipment and human resources.

Today, it can be used to carry out the main stages of nano-device fabrication: lithography (optical, direct laser writing and electron beam), etching (wet and dry), and deposition (metallic via electron beam and dielectric via plasma). It also provides characterization tools (optical and scanning microscopies, profilometry, atomic force microscopy and electrical characterization). Finally, our cleanroom offers the capability to develop unique processes within a nanofabrication line compatible with ultra-high vacuum for nanosciences, including the fabrication of ultra-small epitaxial nanostructures, molecular systems, and nano-machines. For example, we can cite the micro-stencil through suspended diaphragms, achieving the required quality for studies with picometric precision necessary for investigating atomic circuits and molecule-machines under UHV-STM.

The efforts of our cleanroom staff have allowed us to achieve our objectives in terms of human resources this year, thanks to CNRS support. A research engineer has been recruited to manage our cleanroom, supported by a team of five staff members, including two working full-time and three part-time.

On the Toulouse site, we aim to collaborate with clean rooms at LAAS and AIME based on technical complementarities, as well as with the Exfolab platform established at INSA by LPCNO and LNCMI. Beyond this, when necessary, the team relies on the resources available within the national RENATECH network of technological facilities, a network we wish to join as a local second-tier center.

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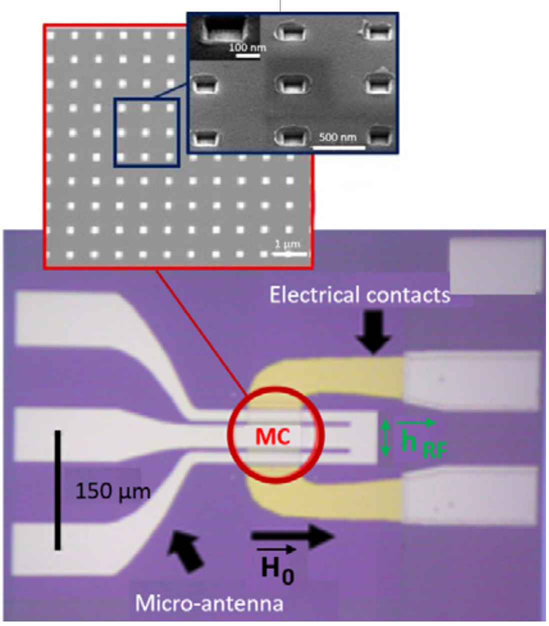
Example of a device entirely fabricated at CEMES as part of Sarah Mantion's PhD thesis (defended in 2023). The magnonic crystal (MC) is a 2D antidot lattice in a thin layer of Co_2MnSi (produced at CEMES), addressed with electrical contacts (DC current) and micro antenna for RF spin wave modes excitation and measurements.



SÉBASTIEN WEBER, 2024 LAUREATE OF THE CNRS CRYSTAL MEDAL*

@David Villa SCIENCEIMAGE CBI CNRS

During his studies at ENS Cachan, Sébastien Weber developed a passion for non-linear optics. He devoted his thesis and several post-doctorates to this field, developing an interest in instrumentation. This led him to seize the opportunity to join CEMES as a research engineer in nano-optical instrumentation.

Today, Sébastien Weber has a dual role in the laboratory: he manages the optical spectroscopy department and designs instruments to meet the specific needs of his colleagues. Among his achievements, he has developed a Kerr microscopy system, a technique that uses light to analyze the magnetic properties of materials. He has adapted its capabilities to enable measurements on a microscopic scale.

Sébastien Weber appreciates the freedom he has to create innovative instrumentation solutions, from experimental benches to software such as PyMoDAQ. This open source interface project, which came into being during his post-doctoral studies, aims to provide a modular system for automating data collection on any experimental devices. Today, PyMoDAQ is used by researchers working in particular on ultrafast microscopy, spectroscopy and attosecond physics. At the end of 2024, it was awarded the Open Science Prize for free research software. At the same time, Sébastien Weber is actively involved in raising awareness and training scientific communities in the use of this collaborative tool, while continuing to improve it through a development project supported by CNRS Innovation.

For all his work, Sébastien Weber has been awarded the CNRS Crystal Medal.

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**The Crystal Medal is awarded to CNRS engineers, technicians and administrative staff who, through their creativity, technical expertise and sense of innovation, contribute to the advancement of knowledge and the excellence of French research.*

THE CEMES COMMITS TO REDUCING GREENHOUSE GAS EMISSIONS

In 2024, the CEMES adopted a series of measures to reduce its greenhouse gas (GHG) emissions, aiming for a 55% reduction by 2030 compared to the 2019 baseline.

The initial GHG assessment, conducted for 2019, reported total emissions of 1,651 tonnes for the laboratory, equivalent to 11.1 tonnes of CO2 per person. The primary contributors were purchases (40%), followed by buildings (25%) and professional travel (15%). In subsequent assessments, apart from the drop in travel in 2020 and 2021 due to the COVID pandemic, these trends remained consistent (see figure).

Starting in 2022, various measures were proposed to raise staff awareness (seminars, promoting cycling for commuting, etc.), begin insulating buildings, and reduce electricity and gas consumption.

In 2024, for purchases and business trips, the laboratory implemented a multi-phase approach to reduce emissions. After a consultative vote in 2023 on 30 proposed measures, 13 were selected for further development. In the second phase (from July 2023 to May 2024), a working group refined these selected measures to make them applicable to the laboratory. The decision-making process culminated in a presentation of the measures at a general assembly, followed by an online consultation with staff, who validated them. The laboratory board then formally approved the measures.

Measures include:

- **Purchases**: Focusing on second-hand equipment, sourcing from local and sustainable suppliers, and coordinating collective orders.

- **IT Equipment**: Extending the lifespan of devices, creating a resource center for reuse, and setting limits on screen resolution for new acquisitions.

- **Travel**: Promoting train travel for trips under 5 hours, restricting long-haul flights to one per person annually and medium-distance flights to three per person annually, with an eco-contribution applied for exceeding these limits.

These measures aim to minimize the laboratory's environmental footprint while preserving its commitment to research excellence. Their success depends on the collective efforts of all members of the laboratory community, including researchers, staff, and students.

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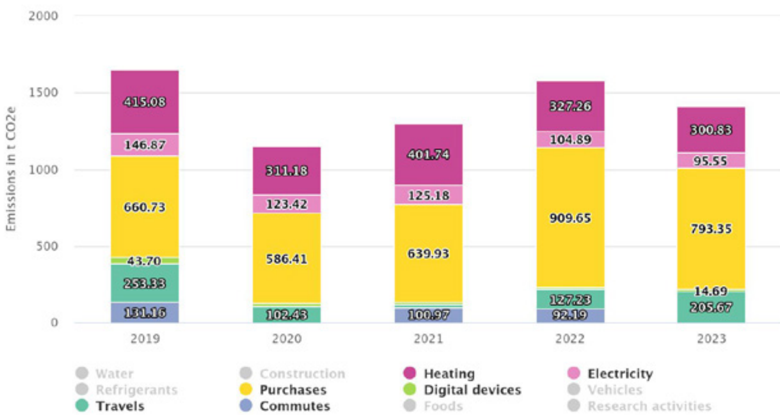

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