INSTITUT JEAN LAMOUR

HIGHLIGHTS 2021

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UNIVERSITÉ DE LORRAINE

CONTENTS

FOREWORD

The Covid 19 pandemic has left its imprint on 2021. People of our institute have been deeply affected by the lockdown period and even by its ending, when everyone had to go back to a daily routine that was anything but ordinary. Almost all conferences, all teachings, all meetings were attended online, an exercise we finally got trained to, without getting used to it.

COP 26 reaffirmed, once more, the need for a swift change of our carbonated lifestyles. IJL decided to ban the use of airplanes whenever it is possible to travel by train in less than 8 hours (i.e. any place in metropolitan France but Nice and Corsica, and any destination in Europe fulfilling this criterium). This crowning decision was taken with a bunch of others of ecological significance: optimizing the operating methods of the laboratory, promoting the acquisition of long-life equipment or sensitizing our institutions to the lack of relevance of some criteria used for promoting researchers, like the number of invited conferences. All these decisions were approved by the IJL's sustainable development committee.

In 2021, we benefited from a unique national momentum that led us to apply to many specific calls in addition to recurring ones: PIA4 (fourth Investments for the Future Programme), Plan France Relance (France Recovery Plan), renewal of the CPER (State-Region project contract), renewal of Lorraine University of Excellence and LPPR (Act on pluriannual Research Programming). IJL was supported in all of these programs.

To mirror the activity of this one-of-a-kind year, a dozen publications were selected. They illustrate the wide scope of our IJL's studies in the field of materials, a multi-disciplinary approach that is the hallmark of our institute.

IJL is also known to support industry through collaborative partnerships. The inception of a new joint laboratory, named MOLIERE, with the Dassault group, together with our colleagues from IPCMS in Strasbourg, marks the coming of a long-term collaboration. This is the same kind of backing the industry of metallurgy expected from IJL with the creation of a chair in solidification. Five industrial groups pooled their common interest in this scientific domain to maintain the excellence of this activity, essential for long-term objectives.

2021 was also the year of the beginning of the SPEKTRE project: Sheaths, Plasma Edge & Kinetic Turbulence Radio-frequency Experiment. Designed with the support of IPP Garching to be a world-open research platform dedicated to plasma physics under intense magnetic fields, this new large reactor will be used for studies related to thermonuclear fusion or surface treatments under magnetized plasma.

For the first time ever, 3D-printing of permanent magnets was made possible thanks to a collaboration between 2 IJL groups, specialists of 3D-printing and magnetism. The process will be marketed by the French company BBFil. This remarkable result opens the way to 4D-printing of magneto-active objects, which can be deformed, activated or controlled by a magnetic field.

A national media impact shed light on our contributions to the knowledge of medieval mortars on the site of Notre-Dame de Paris and to the recycling of metals in used mobile phones. The issues of the importance of materials in our every-day life and of their sustainability is a crucial point that worries consumers and challenges the researchers that we are.

Much has to be mediated in this field and, in this sense, the laboratory launched its brand new website: https://ijl.univ-lorraine.fr

2021 was rewarding in many ways. With the personal commitment of IJL's staff and the unwavering support of the CNRS and the Université de Lorraine, our trajectory was finally made sustainable beyond another difficult year. And this, undoubtedly, is the kind of hope we must nurture.

Thierry Belmonte
Head of Institut Jean Lamour

2D materials

DISPERSING AND SEMI-FLAT BANDS IN THE WIDE BAND GAP TWO-DIMENSIONAL SEMICONDUCTOR BILAYER SILICON OXIDE

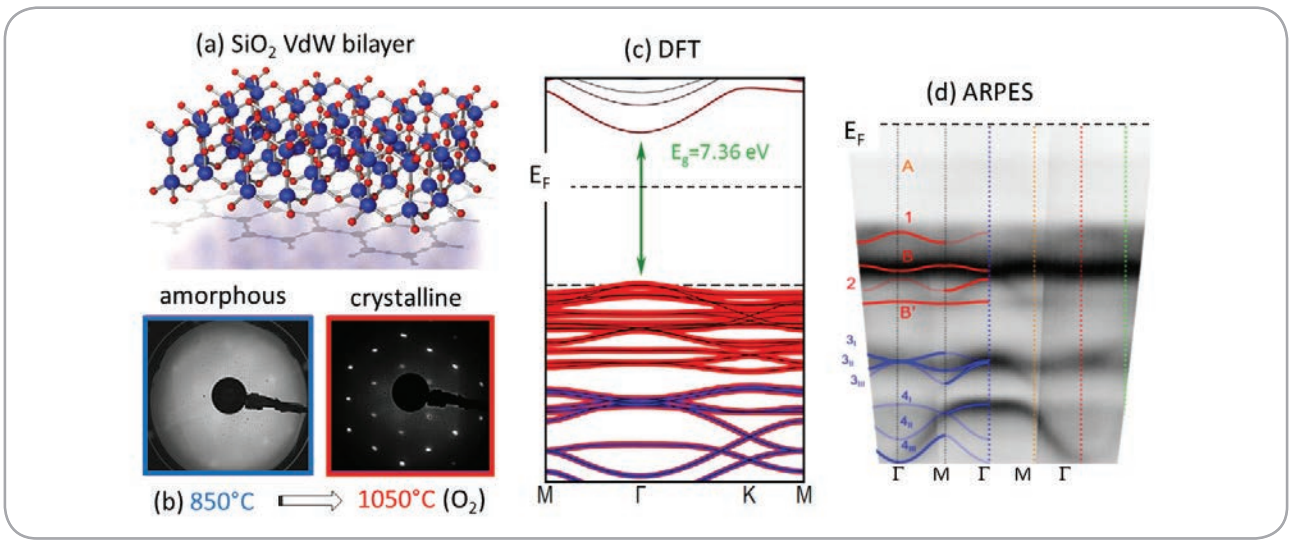
Epitaxial bilayer silicon oxide is a transferable two-dimensional material predicted to be a wide band gap semiconductor, with potential applications for deep UV optoelectronics and as a building block of van der Waals heterostructures.

The prerequisite to any sort of such applications is the knowledge of the electronic band structure, which our resarchers unveiled using angle-resolved photoemission spectroscopy and rationalized with the help of density functional theory (DFT) calculations.

Our researchers discovered dispersing bands related to electronic delocalization within the top and bottom planes of the material, with two linear crossings reminiscent of those predicted in bilayer AA-stacked graphene, and semi-flat bands stemming from the chemical bridges between the two planes.

This band structure is robust against exposure to air, and adjustable by exposure to oxygen.

An experimental lower-estimate of the band gap size of 5 eV was provided and predicts a full gap of 7.36 eV using DFT calculations.



(a) Structure of the 2D vdW SiO_2 bilayer, (b) LEED patterns obtained on the glassy and 2x2 SiO_2 bilayer elaborated on a Ru(0001) substrate, (c) Theoretical band structure obtained by DFT calculations, (d) Corresponding ARPES spectra measured along the M-Γ-M high symmetry direction of the 2x2 surface Brillouin zone

Reference:

Dispersing and semi-flat bands in the wide band gap two-dimensional semiconductor bilayer silicon oxide
Geoffroy Kremer, Juan Camilo Alvarez-Quiceno, Thomas Pierron, César Gonzalez, Muriel Sicot, Bertrand Kierren, Luc Moreau, Julien Rault, Patrick Le Fèvre, François Bertran, Yannick Dappe, Johann Coraux, Pascal Pochet and Yannick Fagot-Revurat
2D Materials, April 2021
https://hal.archives-ouvertes.fr/hal-03218918

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Bio-sourced materials

MODEL CARBON MATERIALS FOR SUPERCAPACITOR ELECTRODES

Model porous carbons with either totally disordered or totally ordered mesostructure, but showing negligible differences in all their other textural and physicochemical properties, have been prepared at the Institut Jean Lamour.

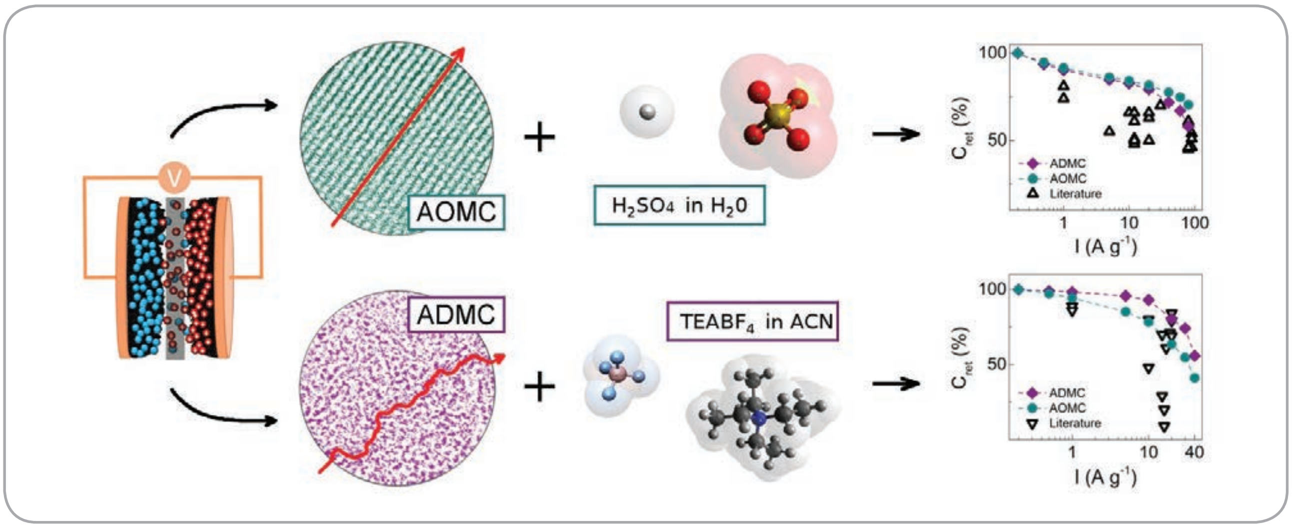
Our researchers worked in collaboration with two CSIC laboratories in Spain: the Institute of Carbochemistry in Zaragoza and the Carbon Institute in Oviedo. These materials were prepared by mechanosynthesis from tannin and block copolymers, followed by carbonization and activation with CO_2.

Using an original technique applied to nitrogen adsorption-desorption isotherms, the hysteresis loop scanning, it was possible to better understand the pore network connectivity and relate it to the electrochemical performance of these materials when used as supercapacitor (SC) electrodes.

It has been shown that an ordered structure is more favorable for the diffusion of aqueous electrolytes, whose ions are small, while the better connectivity of the pore network of the disordered structure improves the diffusion of organic electrolytes, whose ions are larger. Better electrochemical performance is thus achieved for each case.

A thorough review of the literature concluded that the carbons developed here are a fast, low-cost and environment-friendly alternative for use as electrodes in SCs. This approach will contribute to the optimization of electrode materials for SCs.

The first author, Jimena Castro-Gutierrez, developed this work in our laboratories thanks to the grant awarded by the prestigious CONACYT-SENER program of the Mexican government. After her thesis defense in 2020, she continues her research at IJL thanks to the TALiSMAN project co-financed by the ERDF.



Left, scheme of a supercapacitor using ordered (green) or disordered (purple) porous carbon materials as electrodes. These ordered or disordered carbons perform remarkably well with aqueous and organic electrolytes (center), respectively, when comparing the capacity retention as the current density increases (right figures).

Reference:

Model carbon materials derived from tannin to evaluate the importance of pore connectivity in supercapacitors
Jimena Castro-Gutiérrez, Noel Díez, Marta Sevilla, M.Teresa Izquierdo, Alain Celzard, Vanessa Fierro
Renewable and Sustainable Energy Reviews, August 19, 2021
https://doi.org/10.1016/j.rser.2021.111600

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Electric arcs

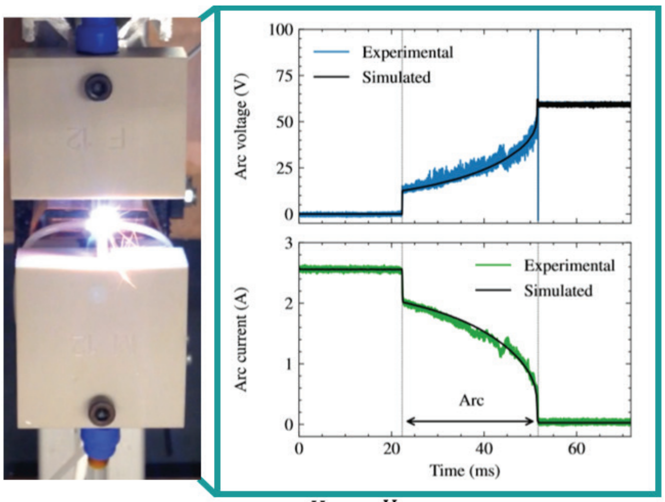
STATE-SPACE SIMULATION OF ELECTRIC ARC FAULTS

The numerical simulation of faults in electrical networks or in electrically powered devices, to ensure reliability, is not new. Researchers have been considering more intensively over the last 10 years a particular problem of low voltage AC and new DC electrical networks. This concerns electric arcs appearing in an untimely way in series with an electric load.

These faults are the consequence of many situations, the most common of which are a contact fault on a connector or a power supply terminal block, and the ageing of power cables. The numerical simulation of these faults represents a real difficulty in the sense that electrical models are often not very accurate to study the electrical disturbances generated in the network. These models must also be compatible with electrical network simulators. The aeronautical industry considers continuous networks of 540 V in order to move towards the more electric aircraft. Fault simulation is even more crucial for these networks' safety.

Fault detection relies increasingly on artificial intelligence (AI) techniques embedded in aeronautical circuit breakers (AFCB). The training of these AI requires a large amount of accurate and realistic fault data in complex networks. However, the cost to produce these data is very high in terms of equipment and time. Thus, simulated data is an essential complement to experimental data.

Modeling the different elements of the network (loads) by state-space formalism is a common way to simulate electrical networks. Thus, the proposal is to use this formalism on an electrical model of arc faults that our researchers had proposed in a previous paper. This way the model is compatible with the classically used simulators. The paper also presents the excellent agreement between the experimental results and the simulation model.



$$\begin{cases} I_k = -\dfrac{V_{k-1}}{R} + \dfrac{V_{g_{k-1}}}{R} \\ V_k = \dfrac{mF(I_{k-1}) + V_{k-1}}{(1+m)} \end{cases}$$

Image of a DC series arc with an RL load generated by contact opening with aeronautical contact, the model equations and the comparison between simulated and experimental arc voltage and current

The work carried out in collaboration between IRT Saint-Exupéry (Toulouse) and IJL (Measurement and Electronic Architectures group) is based on the development of a simulated arc fault model using the state-space representation formalism, according to Andrea's arc model.

This work was partially funded by the Clean Sky 2 Joint Undertaking (JU) under grant agreement N° 101007868. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Clean Sky 2 JU members other than the Union.

Reference:

State-space simulation of electric-arc faults
A. Chabert, P. Schweitzer, S. Weber and J. Andrea
IEEE Transactions on Aerospace and Electronic Systems, October 2021
https://doi.org/10.1109/taes.2021.3118962

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Graphene

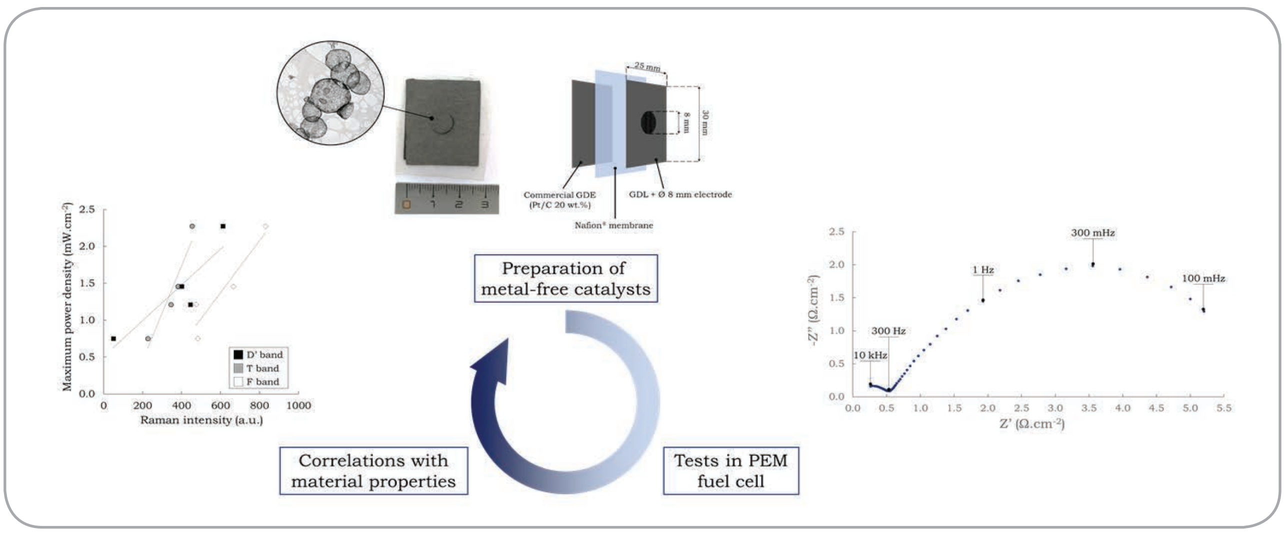
METAL-FREE NITROGEN-DOPED GRAPHENIC MATERIALS AS CATHODE CATALYSTS FOR THE OXYGEN REDUCTION REACTION IN POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

Exhibiting a very high surface area, a good electrical conductivity and a high density of active sites, nitrogen-doped graphenic materials is considered as promising catalysts for the oxygen reduction reaction in polymer electrolyte membrane fuel cells.

The storage of energy in the form of dihydrogen is attracting growing interest in the scientific community as well as in the energy and transport industries. Proton exchange membrane fuel cells (PEMFC) convert this gas into electricity without harmful emission, at relatively low temperatures. Nowadays, catalysts are mainly made up of platinum nanoparticles, deposited on a microporous carbon material. However, this noble metal is a source of environmental and societal problems, and its supply is subject to geopolitical tensions and vagaries. This paper explores the possibility of using alternative materials without metals.

Widely studied in the literature, carbon materials doped with nitrogen atoms have a catalytic activity for the oxygen reduction reaction (ORR), this reaction being the most limiting in PEMFCs. An elaboration method based on a solvothermal reaction between an alcohol and sodium, followed by a pyrolysis treatment, has been developed, yielding N-doped graphenic materials with a pronounced three-dimensional aspect and a very developed porosity.

The catalytic activity of doped graphenic materials has been proven inside a PEMFC using chronopotentiometry and impedance spectroscopy, depending on the synthesis conditions. Relationships between the electrochemical behavior of the materials and their structural properties were discussed. Moderately crystallized materials with a low oxygen content showed the highest catalytic properties, with a current density larger than 30 $mA.cm^{-2}$ and a maximum power density at 2.3 $mW.cm^{-2}$.



The properties' optimization of nitrogen-doped graphene materials used as noble metal-free catalysts leads to very promising performances

Reference:

Metal-free nitrogen-doped graphenic materials as cathode catalysts for the oxygen reduction reaction in polymer electrolyte membrane fuel cells
L. Moumaneix, S. Fontana, C. Hérold, F. Lapicque
Journal of Applied Electrochemistry, February 2021
https://doi.org/10.1007/s10800-021-01532-6

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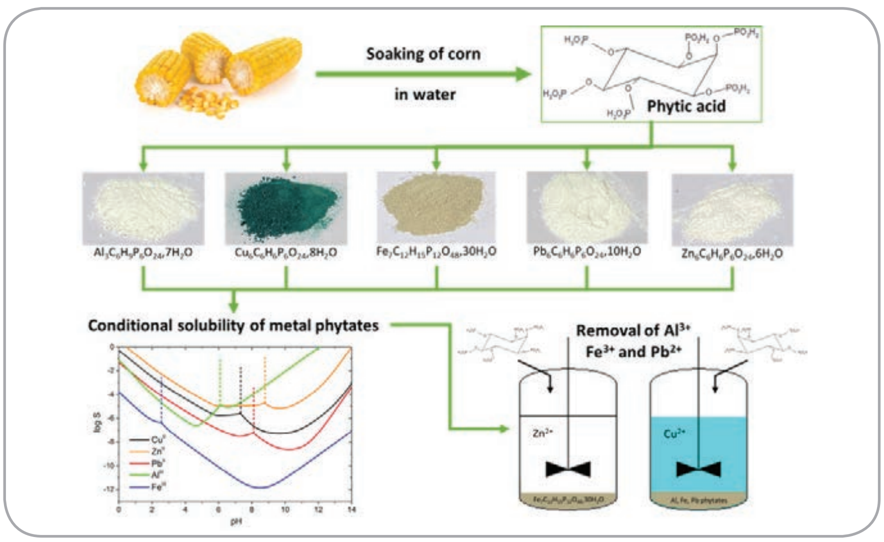
Hydrometallurgy

USE OF PHYTIC ACID FOR SELECTIVE PRECIPITATION OF UNDESIRABLE METALS CONTAINED IN THE LEACHATES FROM HYDROMETALLURGICAL PROCESSES

Chemical precipitation is the most common technology to purify hydrometallurgical leachates before the recovery of the metal of interest either in valuable mineralogical forms (hydroxides or carbonates) or in metallic form after electrolysis. The use of various bio-sourced compounds appears in the literature. These green reactants can be extracted or synthetized from agri-resources such as fatty acids, non-toxic compounds extracted from vegetable oils.

Julien Comel, who defended his PhD thesis on 28 January 2021, studied the possibility to use phytic acid (or myo-inositol-1,2,3,4,5,6-hexakisphosphate) as selective precipitation reagent to remove Al^{3+}, Fe^{3+} or Pb^{2+} from industrial leachates. This acid, which represents 80% of phosphorus contained in plants (cereals, fruits and vegetables), is well known for its ability to form soluble complexes and precipitates with many metal cations such as Ca^{2+}, Fe^{3+} or Zn^{2+} decreasing the absorption of nutrients and their bio-availability in the organism by human body. Considered as an antinutrient, agri-food industry tries to reduce or eliminate a large part of this compound from cereals by soaking them in water. Soaking waters containing between 0.5 and 2 wt.% of phytic acid are considered as non-hazardous waste and are used in agricultural spreading for organic soil amendment. So, this acid was studied as a bio-sourced precipitation reactant to perform "green" hydrometallurgy.



Principle of use of phytic acid to remove Al^{3+}, Fe^{3+} and $Pb2+$ from hydrometallurgical leachates

Thermodynamic data concerning metal phytates are rare in the literature. Therefore, our researchers determined the formula of five phytates (aluminium, copper, iron, lead and zinc), then measured their solubility in order to calculate solubility product Ks. From these data, they established the solubility domain of each metal phytate in order to evaluate the possibility to perform selective precipitation with this reagent. Two potential applications in the field of hydrometallurgy were identified: removal of iron in hot acidic leachate from calcines in zinc extractive metallurgy and removal of Fe^{3+}, Al^{3+} and Pb^{2+} from copper-rich Printed Circuit Board nitric leachates. In the case of calcines leachates, the results observed are better than those obtained by the classical industrial processes such as "Jarosite process". As for nitric leachates from Printed Circuit Boards, Al^{3+}, Fe^{3+} and Pb^{2+}, they are removed with yields higher than 98% without co-precipitate more than 2% of Cu^{2+} cations.

Reference:

Use of phytic acid for selective precipitation of undesirable metals (Al, Fe, Pb) contained in the leachates from hydrometallurgical processes
Julien Comel, Eric Meux, Nathalie Leclerc and Sébastien Diliberto
Journal of Environmental Chemical Engineering, April 2021
https://doi.org/10.1016/j.jece.2021.105450

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Metamaterials

JANUS ACOUSTIC METASCREEN WITH NONRECIPROCAL AND RECONFIGURABLE PHASE MODULATIONS

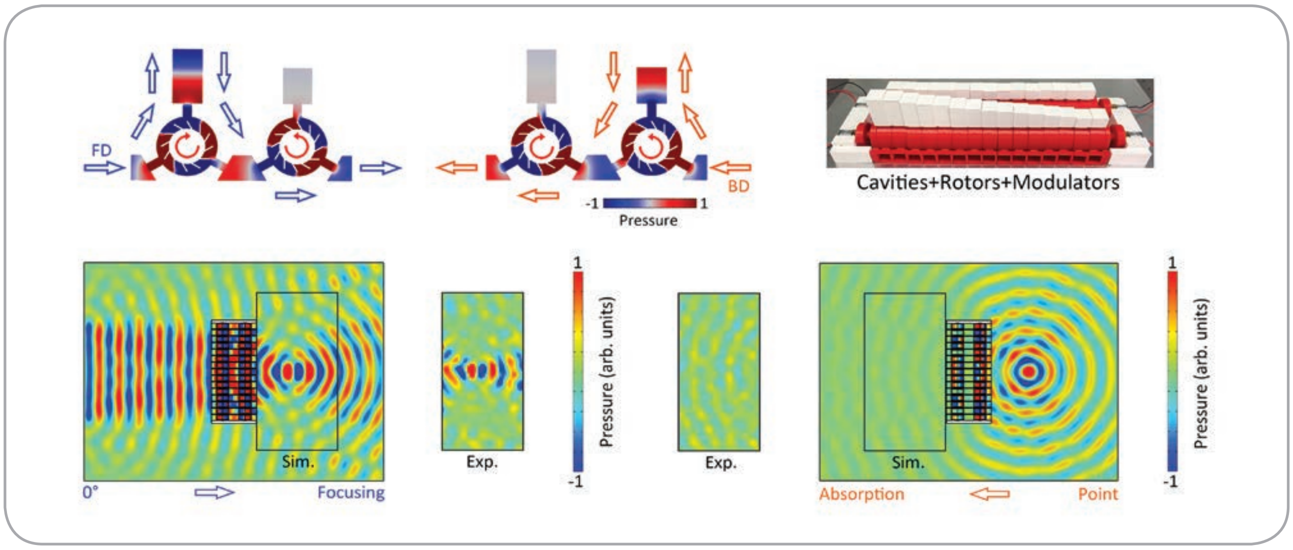
Integrating different reliable functionalities in metastructures and metasurfaces has become of remarkable importance to create innovative multifunctional compact acoustic, optic or mechanical metadevices. In particular, implementing different wave manipulations in one unique material platform opens an appealing route for developing integrated metamaterials.

Inspired by the "god Janus" analogy, in this work, our researchers have introduced the concept of Janus acoustic metascreen for independent wavefront manipulations for two opposite incidences, producing two-faced and independent wavefront manipulations for two opposite incidences.

They have used acoustic resonators with rotating inner cores to achieve high non-reciprocity, and demonstrate tunable combinations of wavefront manipulations. A series of Janus acoustic metascreens including optional combinations of negative refraction, acoustic focusing, sound absorption, acoustic diffusion, and beam splitting have been demonstrated through numerical simulations and experiments, showing their great potential for acoustic wavefront manipulation and structuration.

In this proposed research, completely achieved by the Metamaterials and Phononics group of IJL, the researchers put forward numerical and experimental approaches and analyses to demonstrate the unprecedented concept of Janus acoustic metascreen for wave manipulation and structuration.

Their finding opens a new route for non-reciprocal and Janus acoustic metadevices for myriad of multifunctional and compact systems as well as related applications.



The concept of Janus acoustic metascreen. The numerical simulation of the wave front structuration, and experimental evidence of focusing and absorption functionalities produced under incidences from the two sides of the metascreen

Reference:

Janus acoustic metascreen with non-reciprocal and reconfigurable phase modulations
Yifan Zhu, Liyun Cao, Aurélien Merkel, Shi-Wang Fan, Brice Vincent and Badreddine Assouar
Nature Communications, December 2021
https://doi.org/10.1038/s41467-021-27403-4

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Nanocomposite membrane

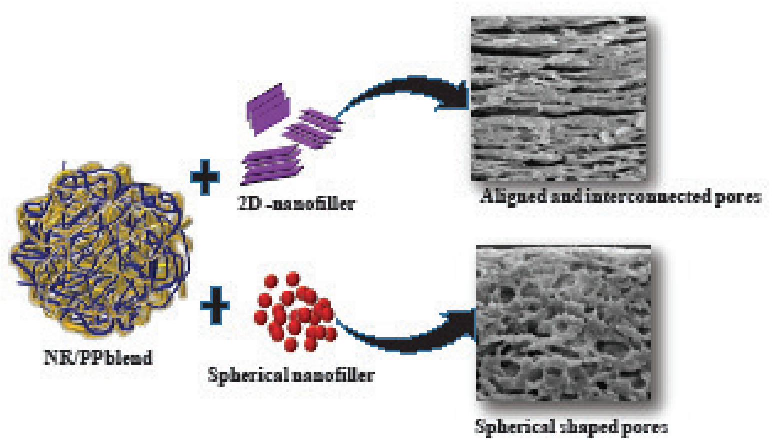
INTERFACIAL TUNING AND DESIGNER MORPHOLOGIES OF MICROPOROUS POLYPROPYLENE / NATURAL RUBBER NANOCOMPOSITES

Microporous polypropylene (PP) nanocomposite membranes are in great demand in various fields such as energy harvesting, water purification and other industrial applications. The pore morphology, mechanical strength and thermal stability of microporous PP is greatly influenced by the morphology and surface area of nanofillers.

Polypropylene is a commodity polymer well-known for its excellent properties and low production cost. Flexible microporous PP membranes with tunable porosity and pore size find application in various fields. Hence studies on the inclusion of nanofillers and its impact on the morphological thermal and mechanical properties porous PP membranes is significant.

This is a collaborative work jointly carried out between Mahatma Gandhi University (Kottayam, Kerala, India) and Institut Jean Lamour, (Didier Rouxel, Micro and Nanosystems group, Isabelle Royaud and Marc Ponçot, Physics, Mechanics and Plasticity group).

In this work, four different types of nanofillers with different surface area and morphology (Cloisite-30B, fumed SiO_2, Al_2O_3 and TiO_2) were introduced in the PP/NR blend by melt mixing method. The extraction of NR phase leaves pores in PP matrix. The effect of nanofillers on pore morphology, pore size, thermal and mechanical properties of PP was evaluated.



Schematic representation of influence of nanofillers on the pore morphology of microporous polypropylene

From this work, it is obvious that the nanofiller morphology and its localization greatly affect the pore size and pore morphology. The platelet shaped nanoparticle creates elongated interconnected pores in PP matrix whereas spherical shaped nanofillers create pores which are almost spherical in shape.

The study reveals that the surface area also influences the properties of PP: greater the surface area of nanoparticles is, greater the filler-polymer interaction will be. Therefore, this limits the polymer chain mobility and improves the mechanical properties of microporous PP.

It is also obvious that the nanofiller morphology and surface area affect the thermal stability and rate of thermal degradation of PP. As a consequence one can tune the properties of this polymer through the proper selection of nanofillers.

Reference:

Interfacial tuning and designer morphologies of microporous membranes based on polypropylene/natural rubber nanocomposites
Kottathodi Bicy, Didier Rouxel, Marc Ponçot, Isabelle Royaud, Patrice Bourson, David Chapron, Nandakumar Kalarikkal and Sabu Thomas
Journal of Applied Polymer Science, June 2021
https://hal.univ-lorraine.fr/IJL-UL/hal-03405714

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Phase transformations

INSIGHTS INTO THE SELECTION MECHANISM OF WIDMANSTÄTTEN GROWTH BY PHASE-FIELD CALCULATIONS

Widmanstätten microstructures have been observed first in iron meteorites at the beginning of 19th century. Quoting French intellectual Roger Caillois, Widmanstätten patterns are "les seuls dessins que l'homme connaisse, qui ne soient pas terrestres". In fact, these fascinating and beautiful microstructures can also be observed in many metallic alloys featuring an allotropic transformation, such as steels, brass or titanium alloys. Hence, beyond their aesthetical value, understanding how they grow is of great interest for predicting the mechanical properties of the concerned metallic alloys.

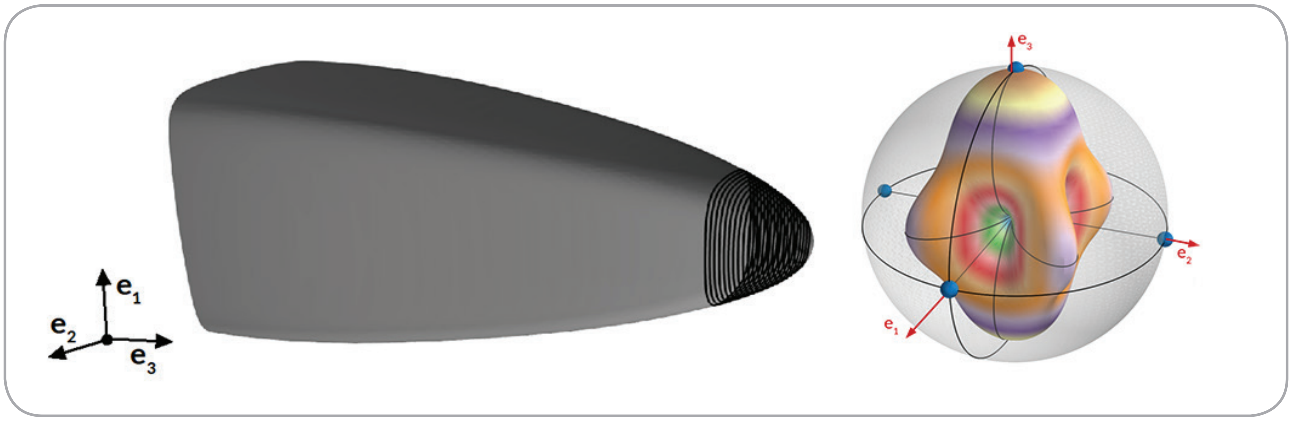
In a joint work between IJL and Laboratoire d'Étude des Microstructures (Onera-CNRS), the researchers have addressed the long-standing problem of the lengthening of the Widmanstätten plates and needles.

It has been assumed for more than 70 years that the process is like dendrite growth during solidification, where both diffusion of chemical species and anisotropic interface energy control the tip size and velocity.

However, the researchers have shown that the elastic distortion associated with the change in lattice structures cannot be neglected as usual, because its anisotropy plays the major role in the growth process. Indeed, it selects the fastest growth direction, as well as the tip size.

Moreover, the researchers have shown that the tip size and shape are not selected dynamically as in dendrites but are simply equilibrium features.

This conclusion constitutes a major outcome in metallurgy because it paves the way for rationalizing the measurements in all alloys featuring Widmanstätten microstructures.



Left: Widmanstätten needle computed by the phase field model.
Right: Elastic energy associated with the orientation of the Widmanstätten structure explaining that lengthening proceeds along the direction featuring the largest elastic energy

Reference:

Insights into the selection mechanism of Widmanstätten growth by phase-field calculations
H. Lebbad , B. Appolaire , Y. Le Bouar, A. Finel
Acta Materalia, September 2021
https://hal.univ-lorraine.fr/IJL-UL/hal-03333692v1

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Plasma

CALCULATING THE SHEATH SIZE BY MEANS OF NUMERICAL SIMULATIONS

Particle-in-cell (PIC) simulation is widely used in plasma physics because of its ability to treat effectively a large number of numerical particles – each one of them representing a variable number of real ions and electrons – with a reasonable numerical cost and a good accuracy. It is based on the computation of self-consistent electromagnetic fields on a fixed mesh, followed by the interpolation of the fields at the particles' position and the integration of their motion equations. Applied to the study of plasma-surface interaction, PIC simulations are a useful tool for investigating the plasma sheath formation.

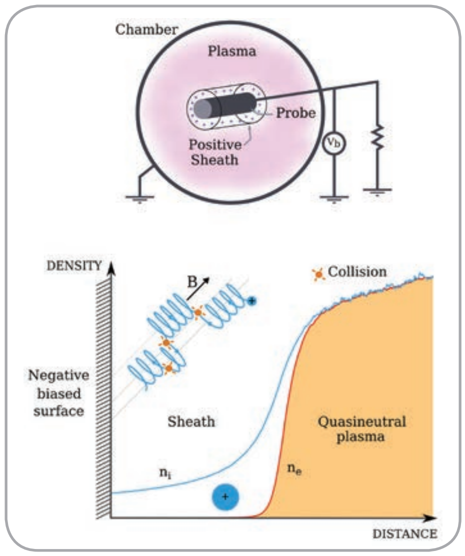
Sheaths are space-charged regions that form at plasma boundaries in order to balance ion and electron losses.

The latter can be an electrode, or the wall of any reactor, and that is why sheath formation is of a paramount importance for many applications in plasma physics.

The kinetic energy gained by ions in the sheath region can be detrimental for fusion reactor walls because of the erosion of their coating and the subsequent pollution of the core plasma.

On the other hand, the same property is extensively used in surfaces processing techniques, from plasma etching to plasma deposition, when the incident ion energy is larger than the one binding the surface atoms together.

Sheaths also arise around Langmuir probes, as shown at the top of the figure. In this case, a bias voltage Vb is applied to an electrode plunged into a plasma in order to record current vs voltage I(V) characteristics.



Sketch of a Langmuir probe plunged into a plasma (bottom) Ion and electron density profiles exhibiting the positive charged region separating the surface from the quasineutral plasma (the sheath)

The lateral extension of the sheath with Vb has been assessed by using PIC simulations, in the presence of a tilted magnetic field B with respect to the collection surface, as depicted in the bottom of the figure. Collisions between ions/electrons and neutral particles have also been taken into account and their effect onto ions and electrons dynamics has shown very interesting features at grazing incidences of B.

For such small angles and high collisionality, ions mobility towards the surface can be larger than the electrons one, because electrons are still forced to move along the field line, whereas ions undergo a random walk perpendicularly to the wall: this can lead to the building of an electro-negative sheath, i.e. an inverted (or anti) sheath.

Exponent relationships between the sheath size and the bias voltage have been calculated thanks to the simulated ion and electron density profiles (see figure), and compared to different models with a relative good agreement, for varying field incidence and collisionality.

This work was supported by the French National Research Agency (ANR) in the framework of SHEAR project and by the Eurofusion consortium and the French Federation for Magnetic Fusion Studies (FR-FCM).

Reference:

Sheath size and Child-Langmuir law in one dimensional bounded plasma system in the presence of an oblique magnetic field: PIC results
J. Moritz, S. Heuraux, E. Gravier, M. Lesur, F. Brochard, L. De Poucques, E. Faudot, and N. Lemoine
Physics of Plasmas, August 2021
https://hal.archives-ouvertes.fr/hal-03215889v2

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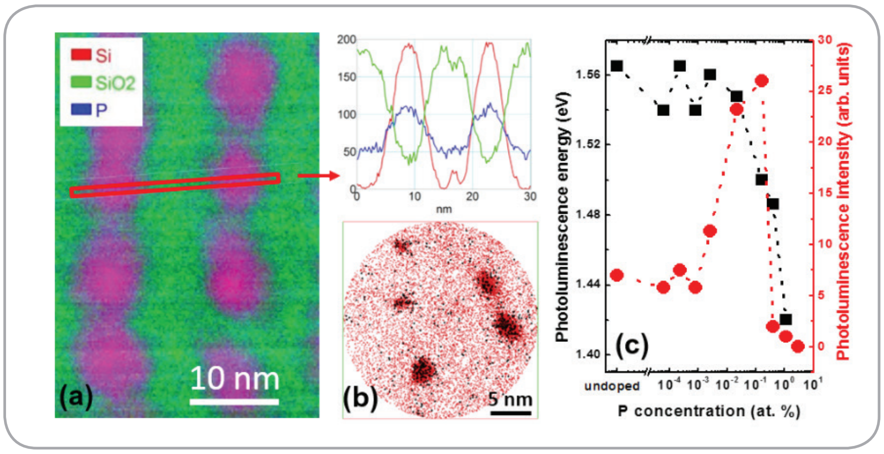
Silicon photonics

DOPING AT THE NANOSCALE: HOW PHOSPHORUS ATOMS INFLUENCE THE OPTICAL PROPERTIES OF CONFINED SILICON NANOCRYSTALS

The collective oscillations of free carriers, also called localized surface plasmon resonances, have been investigated for decades because of their ability to alter light-matter interactions. These oscillations induce an enhanced local absorption and then result in many applications such as optical sensors, photovoltaic devices, or single molecule spectroscopy. If plasmonics was mainly developed from noble metal nanostructures due to their resonance in the visible range, doped semiconductor nanocrystals emerge as promising plasmonic nanostructures mainly because doping and then the free carriers density can be controlled. To reach this tunability, doping of semiconductor nanocrystals needs to be controlled.

This work, resulting from a collaboration between groups of the Skolkovo Institute of Science and Technology, (Moscow, Russia), University of Rouen (France) and Institut Jean Lamour, is focused on the development of model systems for efficient doping at the nanoscale. Size-controlled doped silicon nanocrystals (Si-NCs) were obtained by annealing phosphorus-doped SiO/SiO_2 multilayers, using e-beam co-evaporation of SiO and SiO_2 in ultra-high vacuum under a flow of P atoms produced by a GaP decomposition cell.



(a) STEM-EELS mapping for (SiO/SiO_2):P multilayers annealed at 1100°C with a P content of $6{\times}10^{-2}$ at.%. Si atoms in a Si environment, Si atoms in SiO_2 and P atoms are shown in red, green and blue colors(b) 2D slice view from atom probe tomography showing Si (red points) and P (black points) atoms; (c) Dependence of the photoluminescence peak energy and intensity with the P content

Scanning transmission electron microscopy coupled with electron energy loss spectroscopy and atom probe tomography demonstrate that phosphorus atoms are preferentially localized in Si-NCs. Concentration as high as 10% can be inserted inside Si-NCs. The quantum confinement of carriers in Si-NCs leads to the emission of photons in the near infrared range.

The introduction of P atoms is shown to induce a softening of the SiO_2 matrix leading to the formation of highly luminescent Si-NCs at lower annealing temperatures in comparison with undoped samples and to a photoluminescence (PL) redshift induced by the increase of the Si-NCs size. P doping also leads to an increase of the PL intensity induced by passivation of non-radiative defects at the Si-NCs/SiO_2 interface for average P concentrations below 0.5%. For higher P content, the PL is quenched by electronic levels induced by P atoms in interstitial states or by Auger effect induced by free carriers due to doping. This work established that Si-NCs embedded in a silica matrix are promising nanostructures for plasmonics because of their ability to content a tunable and high quantity of dopants.

Reference:

Influence of phosphorus on the growth and the photoluminescence properties of Si-NCs formed in P-doped SiO/SiO_2 multilayers
Fatme Trad, Alaa Eldin Giba, Xavier Devaux, Mathieu Stoffel, Denis Zhigunov, Alexandre Bouché, Sébastien Geiskopf, Rémi Demoulin, Philippe Pareige, Etienne Talbot, Michel Vergnat and Hervé Rinnert
Nanoscale, November 2021

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Thermoelectricity

HIGH POWER DENSITY THERMOELECTRIC GENERATORS WITH SKUTTERUDITES

Power generation via the Seebeck effect provides an elegant solution to harvest waste heat daily released in our environment. This versatile technology exhibits several advantages in terms of reliability, maintenance- and vibration-free. They make it attractive for space applications (for instance in deep-space probes like Voyager or in Curiosity and Perseverance rovers on Mars), and for numerous industrial areas such as, for instance, powering autonomous sensors.

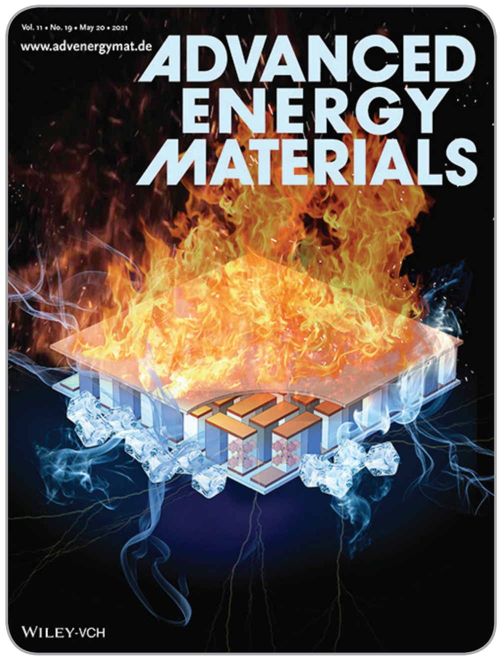
Novel families of efficient thermoelectric materials have been discovered over the last decade. However, their integration into thermoelectric generators have not kept pace due to several issues, notably related to the multiple interfaces between different materials and the significant thermomechanical stresses undergone by the thermoelectric materials. These challenges have so far limited the power densities (expressed in W cm^{-2}) generated by these devices.

To overcome these issues, researchers from IJL have proposed an innovative architecture of the thermoelectric legs that relies on the insertion of thin layers of thermoelectric materials (~1 mm) sandwiched by metallic composites playing the role of buffer layers from a thermomechanical point of view.

The proof-of-principle of this innovative architecture consisted in fabricating thermoelectric generators integrating skutterudites and metallic composites. Power densities largely exceeding previous results (2.1 W cm^{-2}) have been demonstrated with notably a record-breaking value of 7.6 W cm^{-2}, corresponding to an increase of more than 260%.

This novel design, applicable to other families of thermoelectric materials, opens up avenues for the development of a novel generation of high-power-density thermoelectric generators.

This work has been carried out in collaboration with the Fraunhofer IPM in Freiburg (Germany), the Institut de Chimie des Matériaux Paris-Est (ICMPE - CNRS - Université Paris-Est Créteil) and the JPL in Pasadena (NASA, USA).



Art cover for the journal Advanced Energy Materials showing a thermoelectric generator composed of several couples of thermoelectric legs made of semiconducting n- and p-type skutterudites. These couples are connected electrically in series by electrical contacts in copper and thermally in parallel between two ceramic plates. The temperature difference between the two sides of the device generates electrical power via the Seebeck effect.

Reference:

High power density thermoelectric generators with skutterudites
S. El Oualid, I. Kogut, F. Kosior, P. Masschelein, C. Candolfi, A. Dauscher, B. Lenoir
Advanced Energy Materials, April 2021
https://hal.archives-ouvertes.fr/hal-03329225/

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Innovative materials for aeronautics

JOINT RESEARCH LABORATORY WITH DASSAULT AVIATION

In July 2021 a new joint research laboratory (LCR) named MOLIERE (Innovative Functional Materials for Aeronautics) was launched by CNRS, Dassault Aviation and the universities of Lorraine and Strasbourg. This LCR project will tackle on developing new and artificial materials for acoustics, electromagnetism and anti-icing devoted to aeronautics.

MOLIERE is a long-term research partnership (four years renewable) supported by the French Defence Innovation Agency.

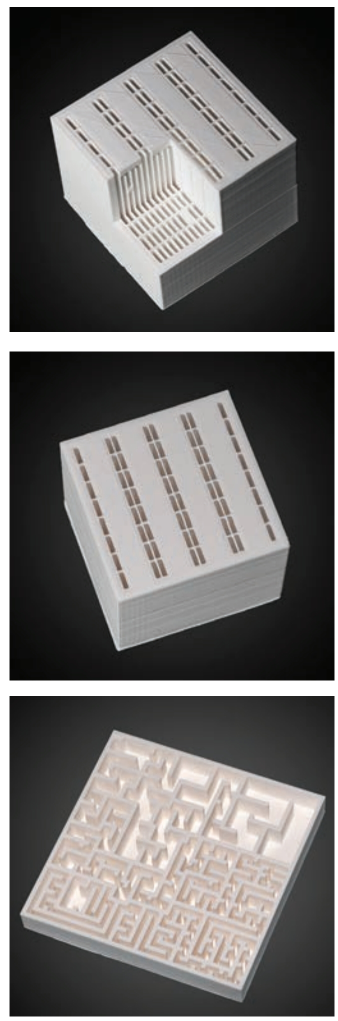
The LCR MOLIERE involves researchers from the Institute of Physics and Chemistry of Materials of Strasbourg (IPCMS) and the Institut Jean Lamour. They will use their modeling and experimental resources and facilities to deal with specific scientific and technological challenges for aeronautics applications.

The LCR is structured in three research axes in which the IJL is involved, with a leadership on the axis of artificial materials for acoustics.

Our experts in metamaterials and phononics will deal with the challenging problem of low-frequency absorption based on ultra-thin metasurfaces which will be used in the business aircrafts manufactured by Dassault Aviation.

The objective is to drastically reduce and absorb the internal low-frequency noises inside the aircraft cabins, which requires the development of innovative, lightweight and high-performance materials with an extremely reduced thickness.

To that end, our researchers explore transformative concepts of acoustic metamaterials and metasurfaces, based on an in-depth physical analysis of the interaction between acoustic/vibro-acoustic waves and propagating media with heterogeneous characteristics.



Examples of acoustic metamaterials and metasurfaces developed at IJL

References:

Watch the short video (in French) about MOLIERE:
https://youtu.be/Ep-4fXECT00
Read the press release (in English):
https://bit.ly/3wn7Dpx

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Metallurgy

AN INDUSTRIAL CHAIR DEDICATED TO SOLIDIFICATION

In July 2021 a third Université de Lorraine industrial chair was launched at the Institut Jean Lamour. It deals with solidification in metallurgy and Jacob Kennedy, its holder, presents the outline and the first results of his project, as well as his own background.

5 industrial partners

This 5-year industrial chair is funded by Arcelor-Mittal, Arcelor-Mittal Industeel, CEA, EDF and Framatome. We are going to work with them to solve a common problem in the manufacture of semi-finished products, such as steel ingots, intended for the energy and transport industries.

During continuous casting or casting of large ingots of steel, a phenomenon of chemical segregation occurs, which can have consequences on subsequent manufacturing processes. In particular, we will seek to model these segregation phenomena, in order to better anticipate them and optimize the subsequent processing stages.

Background in steel research

I am from Edmonton in Canada. After a Bachelor in Materials Engineering at the University of Alberta, I worked in the oil and gas industry primarily concerned with welding engineering and quality control.

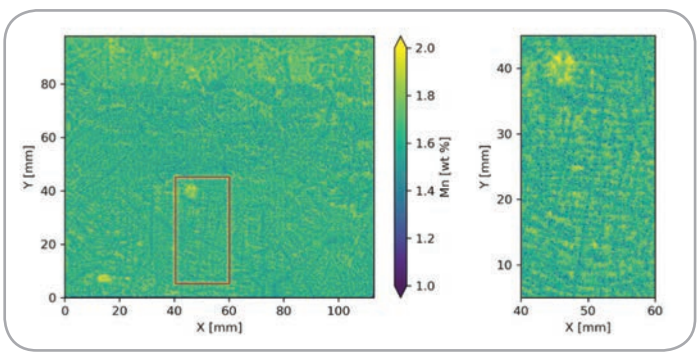
I continued with a master's degree in steel research at the same university, in which I used ultrasound to study the microstructure of steels. The existing links between my professor and IJL allowed me to pursue a doctorate in Nancy within the framework of the LabEx DAMAS, and focus my research on solidification of metallic materials. In 2018, I defended my thesis entitled "Development of a new generation of inoculants for titanium aluminides".
After a 2-year post-doctorate as the project metallurgist for the New Wire Additive Manufacturing project at the University of Manchester, I am back in Nancy, holding the industrial chair within the Solidification group of IJL. The topic of the chair lines up very well with my field of research and the Solidification group at IJL is, in my opinion, one of the best in the world in this field. This is a great opportunity for me to work with its researchers and industrial partners to improve understanding of industrially relevant solidification processes.

Project beginnings

Work on the project of the chair began with recruiting a PhD student, Lucie Gutman. Her project is an academic/industrial partnership, a CIFRE contract, between Framatome and IJL. Conventional characterization techniques are either too coarse, focused on macrosegregation, or too fine, focused on microsegregation, to characterize the important segregation around the large, cm scale, equiaxed grains found during casting of large industrial steel ingots.

She has pioneered the use of micro X-ray fluorescence (µXRF), a technique commonly used in earth-sciences but not metallurgy, to characterize and quantify these intermediate, grain scale chemical inhomogeneities (mesosegregation). The opposite figure shows the first results of her thesis.

We are also happy to welcome Dr. Ahmed Boukellal recruited as a research associate for the chair, who will be working to support the modelling work of Lucie and throughout the project.



Chemical map of Mn over an area greater than 10x10 cm, where a difference in concentration can be seen between the top and bottom of the map, while also still having the resolution that the dendritic structure can be distinguished

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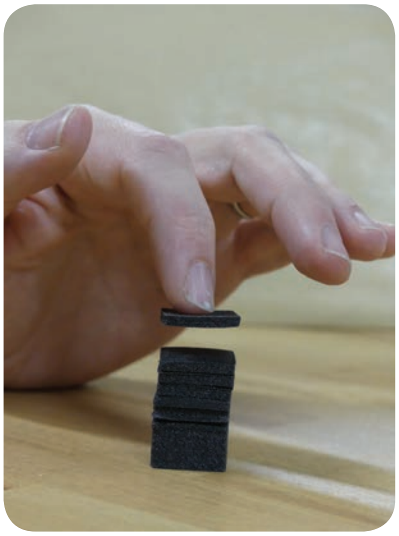
Additive manufacturing

FIRST 3D-PRINTED MAGNETS

Integrating magnetic properties into 3D-printed materials without post-magnetization is a technological challenge that was taken up by our researchers and engineers in 2021.



Pile of 3D- printed magnets

This is an international first with this level of performance and this work opens the way to 4D printing of magneto-active objects. This manufacturing, based on a low cost domestic 3D-printer, is being transferred to a French company.

Technological success

This technological innovation combines the know-how of the IJL' s Materials and Additive Processes group and Magnetism and Cryogenics technical platform.

The challenge faced by our researchers and engineers was to design an FDM (fused depositon modeling) type 3D-printer and a composite magnetic wire able to print magnets.

For the wire they used ferromagnetic materials with specific formulations that would make them printable. As for the printing device, they started from a traditional 3D-printer, to which they added components allowing the magnet's shaping during printing.

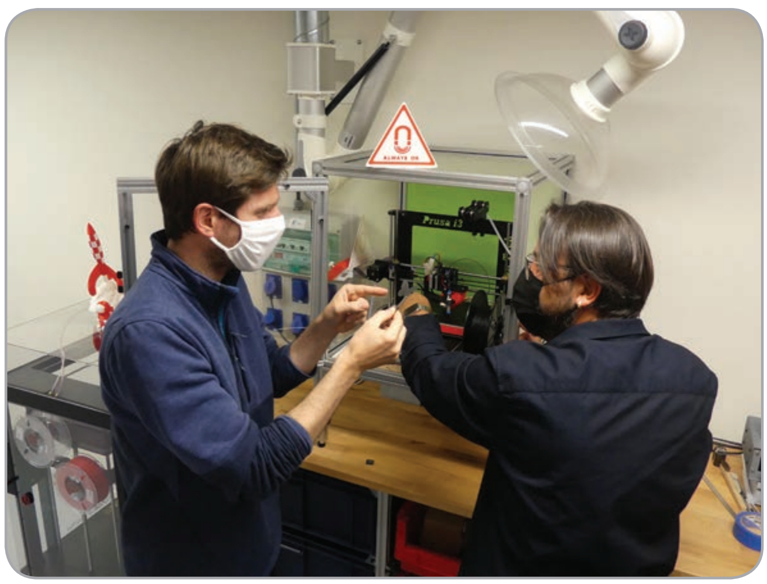
The objects thus printed have one or more permanent magnetic orientation(s) without applying a post magnetic field to magnetize them.

Technological transfer

An invention disclosure was filed in 2019 and the system was optimized until a know-how license agreement was signed with BB Fil company based in Heiligenberg, France, in 2021.

The marketing of a domestic printer and printing filament is planned and will make it possible to print customizable magnets at home.

This work paves the way for 4D-printing of magneto-active objects, which can be deformed, activated or controlled by a magnetic field.



IJL researchers in front of the 3D-printer

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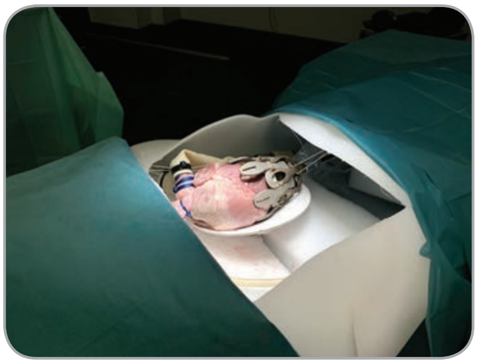
Materials for health

TOWARDS A BIOCOMPATIBLE CARDIAC ASSIST DEVICE

A consortium involving the IJL, the School of Surgery and the University Hospital Center (CHRU) of Nancy has been working on the development of the first biocompatible cardiac assist device. A series of tests carried out *ex-vivo* on animal hearts opens the perspective of an alternative to heart transplantation for patients suffering from myocardial infarction.

This work is carried out within the framework of the 3-year project ASCATIM (Cardiac Assistance for the Treatment of Myocardial Infarction) funded by the European Regional Development Fund (ERDF).

The implantable medical device combines a 3D-printed motorized exoskeleton using titanium powder, designed by the Nancy School of Surgery and two local start-up (Velvet Innovative Technologies and HanaCorps) and a membrane of natural origin developed at the IJL. It will be placed in a minimally invasive way around the failing heart to improve its contractile capacities.



Exoskeleton placed on an explanted porcine heart and simulated in the EXOHEART simulator designed by the consortium

Two work steps were carried out to improve the performance and implantability of this new cardiac assistance device:
• The Nancy School of Surgery has developed, with the University Hospital of Nancy and INSERM, an on-board control system for the exoskeleton. It has the advantage of being energy efficient and of synchronizing with the heart rate of the native heart.
• The IJL has developed the interface membrane between the exoskeleton and the heart. It is a bio-prosthesis, composed of alginate (from seaweed) or chitosan (from cicada or shrimp moulting). The laboratory is also studying the numerical modeling of the heart. The objective is for the membrane to fit the outer contour of the heart by limiting the risks of inflammation and stiffening.

A series of tests has been carried out on a tailor-made platform installed at the Nancy School of Surgery. This platform makes it possible to simulate an *ex-vivo* operation on a heart. Performed on rat and pig hearts, similar to the human heart, these tests have validated the characteristics of cardiac assistance in terms of frequency and pressure. As for the membrane, tests have shown that it can be sutured without modifying the mechanical behavior of the heart.

The functional prototype was the subject of a declaration of invention from the Université de Lorraine and a patent was filed.

The next step consists in testing *in vivo* the implementation of the exoskeleton together with the membrane on a heart that has suffered a myocardial infarction.

References

Transverse isotropic modelling of left-ventricle passive filling: mechanical characterization for epicardial biomaterial manufacturing
J. P. Jehl, P. Dan, A. Voignier, N. Tran, T. Bastogne, P. Maureira, F. Cleymand
Journal of the Mechanical Behavior of Biomedical Materials, July 2021
https://hal.univ-lorraine.fr/IJL-UL/hal-03189522

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Spintronics

STÉPHANE MANGIN APPOINTED FELLOW OF THE CHURCHILL COLLEGE, CAMBRIDGE UNIVERSITY

In August 2021 Stéphane Mangin leader of the IJL's Spintronics and Nanomagnetism group, was invited for a year at Cambridge University, UK, as a visiting scientist and appointed Fellow of the Churchill College.

Stéphane Mangin has been a Professor since 2008 at Université de Lorraine. During the last 15 years, he has focused on magnetization manipulation at the nanometer scale using various stimulus such as field pulse, electric field current pulse and ultra-short laser pulses.

His group demonstrated ultra-fast magnetization reversal of a ferromagnetic layer using a single femto-second laser.

Stéphane is a senior member of Institut Universitaire de France, a fellow of the American Physical Society and a fellow of the IEEE Magnetic Society.

He is the scientific director of a unique tool (D.A.U.M. Tube): a 70-meter tunnel under ultra-high vacuum which connects 30 facilities to grow and characterize materials down to the atomic scale.

At the Churchill College, which is one of the 31 colleges of Cambridge University, with a specific focus on mathematics, science and technology, Stéphane is enrolled within the Microelectronics research group at the Cavendish laboratory. His project is to work on ultra-fast superconducting spintronics.

References:

Full biography: https://en.wikipedia.org/wiki/Stéphane_Mangin
Webpage of the Spintronics and Nanomagnetism group: https://spin.ijl.cnrs.fr
Webpage of the Microelectronics group: https://www.phy.cam.ac.uk

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Heritage

ANALYZING NOTRE-DAME DE PARIS CATHEDRAL'S MORTARS

In 2021 our Materials for Civil Engineering's researchers were allowed to step in Notre-Dame de Paris cathedral's site in order to collect samples from ancient mortars.

This is part of a broad scientific project supported by the CNRS and the French ministry of Culture from 2019 to 2024. The IJL has been chosen alongside 17 other French laboratories to take part in a study of the main materials used to build the cathedral, and, more specifically, stone and mortar.

The overall objective is to understand the building methods of a great Gothic cathedral and draw up a technical identity card as an aid in restoring the edifice.

One of the work phases relates to the archaeological study of the lapidary and mortars collected after April 15, 2019's fire. The collapses following the fire actually unraveled parts of the cathedral which, until then, were not accessible.

In this context our researchers were able to collect samples of thirty different mortars in March 2021. They analyzed them thanks to the characterization facilities available at IJL (optical microscopy, thermogravimetric analysis, fluorescence, diffraction, X-ray tomography, electronic microscopy, etc.) as well as specific techniques used in petrographical identifications.

The objective is to determine the composition of the combinations, in order to know if there has been changes in the mortars over time and if their combinations are similar in every part of the cathedral.

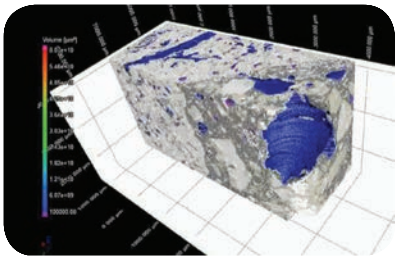
The first analyses of the chemistry of their composition show the mortar of Notre-Dame has proved to be quite uniform and refined for the period.

The manufacture of equivalent mortars makes it possible to better understand the physical properties of the combinations used at the time of construction in the Middle Ages. The results should in particular help to produce an almost identical mortar for reconstruction.

This work is carried out in strong interaction with HISCANT-MA Laboratory (Histoires et Cultures de l'Antiquité et du Moyen-Age) at Université de Lorraine. The "Stone" working group also involves: LRMH - Laboratoire de Recherche des Monuments Historiques; Universities of Clermont-Ferrand, Lille, Aix-en-Provence/Marseille, Bretagne Occidentale; Ausonius Laboratory (CNRS / Université Bordeaux Montaigne), coordinator of the group.

Collect of mortars from the vaults of the choir

Piece of mortar taken from the collapsed transverse arch of the nave



Tomographic 3D reconstruction of a sample

The researchers present the project for the European Heritage Days in front of Notre-Dame de Paris

References:

Watch the short film (in French) produced by CNRS Images:
https://bit.ly/3FiSl9e
Read update on the project (in English) on the CNRS webpage:
https://bit.ly/38Qzrui

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Preservation of the resources

COLLECTING 10.000 CELL PHONES FOR SCIENTIFIC PURPOSES

In the framework of the THYMO* project, our researchers have collected 10.000 worn cell phones in 6 months thanks to a successful media campaign. The aim is to collect as many metals (copper, tin, silver, gold, palladium, tantalum, antimony) as possible contained in their electronic cards, in order to develop a complete and virtuous recycling process through hydrometallurgical treatments.

Campaign visual

This 3-year project supported by Carnot Icéel gathers the know-how of 3 laboratories (GeoRessources, IJL, Laboratoire Réactions et Génie des Procédés - LRGP) and a technical center (CRITT - Techniques Jet Fluide et Usinage - TJFU). It is driven by Eric Meux, associate professor at IJL.

In order to gather the 10.000 cell phones required for the experimental phase of the project, the communication departments of Carnot Icéel, IJL and Université de Lorraine launched a media campaign named "THYMO – My cell phone gives its core to Science".

This campaign was released on the occasion of the World Materials Forum; this international event gathers each year in Nancy, France, CE0s, academic experts and public leaders in order to discuss solutions in the field of materials efficiency for better growth.

It generated more than 20 press clips in the French and international media, including a TV report on France 3 national channel and an interview on RTL national radio station.

The journalists were all the more interested in the project since it includes the potential creation of a local treatment plant in the near future, which would generate employment opportunities in the region.

Thanks to media coverage our research consortium could reach out to the general public as well as the civil society. Individuals started bringing and sending their old cell phones to the laboratories.

Eric Meux during an interview for the French national TV


Optical image of cell phone scraps

Then solidarity-based companies, charities such as Emmaüs, public organizations like SNCF, Pôle Emploi, a penitentiary centre, but also large groups such as Orange or Air Liquide gave quantity of old phones for this research project.

These donations enabled our researchers to gather around 200 kilos of electronic cards, which provides enough raw materials for conducting reliable separation trials.

After being extracted by CRITT TJFU through cut under high-pressure nitrogen, the electronic cards have been pounded by GeoRessources and IJL has started collecting copper through hydrometallurgy.

This project represents an alternative to pyrometallurgy processes currently used, which do not allow the collection of all the metals contained in electronic cards.

*Traitement hydrométallurgique de cartes électroniques de téléphones mobiles (Hydrometallurgical treatment of electronic cards for cell phones)

References:

Watch French national TV report:
https://bit.ly/3w5lAs2
Read article in Spanish in a Mexican media:
https://bit.ly/3PyuFTe

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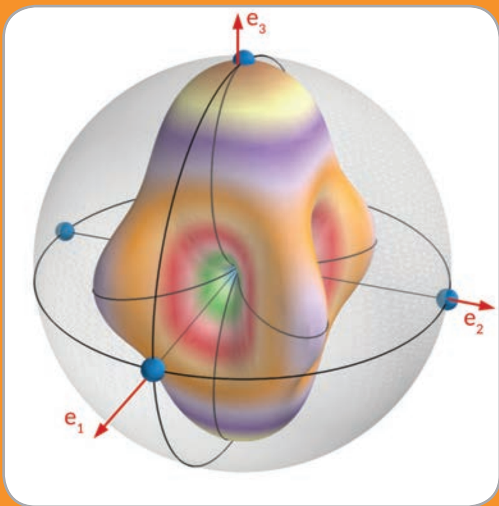

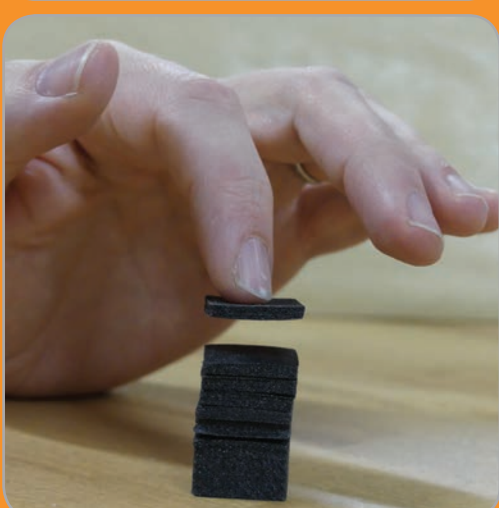

KEY FIGURES 2021

Staff:

167 permanent researchers

59 post-doctoral researchers

177 PhD students

105 support staff

Scientific activity:

298 peer-reviewed articles

64 new research contracts

32 PhD thesis defenses

International:

60 nationalities

200 collaborative actions

30 partner countries

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Production: Communication department of IJL, May 2022 - Cover image: Art cover for the journal Advanced Energy Materials showing a thermoelectric generator composed of several couples of thermoelectric legs made of semiconducting n- and p-type skutterudites.