PhD project proposed at the Institut de Physique de Rennes – International Research Laboratory Dynacom

Department Materials and Light

Title:

Advanced crystallography and ultrafast dynamics studies of charge-transfer based phase transitions

Financial support: CNRS

PhD supervisors: Laurent Guérin (Associate Professor) / Eric Collet (Professor)

State of the art of the research area

Stimulating materials, bringing them into out-of-equilibrium conditions and controlling their properties at the relevant length, time and energy scales is challenging. New technologies based on fs lasers, ranging from THz to X-rays, provide a variety of sources to selectively excite or probe electronic and structural dynamics on their intrinsic time scales. Our goal is to develop ultra-fast controls of complex, coherent, collective or cooperative transformations of molecular materials, which present various functionalities controllable by light (ferroelectricity, magnetism, insulating transition - metal…).[1-3] The field of ultra-fast photoinduced phase transitions is developing rapidly in materials science, in particular for quantum and correlated materials. Pump-probe techniques use a pump laser pulse to prepare the system into a highly excited state, while the real-time induced electronic and/or structural dynamics is tracked with subsequent probe pulses. Molecular materials offer unexplored and attractive perspectives because of their flexibility accompanying changes of electronic state. Cooperative interactions in solids underpinning non-linear responsiveness and threshold response, allows for spectacular triggering of functionalities of materials: insulating to metallic, non-magnetic to magnetic… Crystallographic studies at equilibrium and/or under light irradiation make it possible to study microscopic processes at the crystalline and molecular scale.

Project:

In the frame of the International Research Laboratory "Dynamical Control of Materials" (IRL DYNACOM), which is a shared research laboratory between our department "Materials and Light" at the Institut de Physique de Rennes and the group of Prof. Ohkoshi at the University of Tokyo, our project is to control different classes of photoactive multi-functional materials, like cyanide-bridged bimetallic crystals (M-N-C-M').[4-7] The chemical compositions and structure of newly synthesized cyanide-bridged bimetallic materials, from 0D to 3D coordination networks, result in various properties with rich phase transition diagrams. The most attractive aspect is the charge transfer (CT) between the two constitutive transition metal ions M and M' (such as Co-W), which can give rise to a magnetic order. In addition, the coupled electronic/structural reorganizations are responsible for emergence of various physical properties.[6, 8] The project is to investigate ultrafast photoinduced CT dynamics by combining femtosecond (fs) optical and infrared spectroscopies and to explore the structural trapping process by advanced photocrystallography. We also propose to perform time-resolved X-ray spectroscopy and diffraction at the X-ray free electron lasers (XFEL).[2-3]

For understanding the local, delocalized or propagating processes responsible for optical control of materials from microscopic to macroscopic scales, we will study the propagation of photoinduced CT in various systems forming 0D, 1D, 2D or 3D lattices.[5] Recently, Prof. Ohkoshi's group has prepared cyanido-bridged Co-W materials forming 2D layers and exhibiting room temperature bistability. From a structural point of view, these compounds often exhibit local orders related to their dimensionality that can be probed by X-ray diffuse scattering analysis.[9-10] Our goal is to understand the correlations and local order and photoinduced CT and its cooperative propagation at macroscopic scale. The experiments are carried out at the IPR or on a synchrotron when a more powerful X-ray source is necessary, as well as for ultrafast measurements.

Supervision:

The thesis will be supervised by Laurent Guérin (Associate professor) and by Eric Collet (Professor), who are expert in advanced structural studies of phase transitions, symmetry breaking, and local order (Landau approach, diffuse scattering, 3DΔPDF analysis…).[9-11] This thesis will mobilize other skills of members within the ML department for optical spectroscopy.

L. Guérin has trained many master and doctoral students or post-doctoral researchers in X-ray diffraction and advanced crystallography and supervised two theses. E. Collet was involved in the supervision of 12 Master students, 18 PhD students and 6 postdoctoral fellows, who are co-authors of publications (typically 4-6 per PhD).

The successful PhD student will be trained on optical ultrafast time resolved spectroscopies at IPR as well as on advanced crystallography. The PhD student will exploit the existing crystallography equipment and optical spectroscopy platform at the Institute of Physics of Rennes. The thesis project will benefit from the collaboration networks and international partnerships in place. It will use innovative techniques on site (ultra-fast laser) and on large scale facilities (X-FEL and synchrotron).

This PhD project will be carried out at the Institute of Physics of Rennes and will involve mobility to synchrotron and X-FEL. The work will also be carried out within the framework of the International Research Laboratory DYNACOM piloted by S. Ohkoshi at the University of Tokyo and E. Collet at the University of Rennes. In this context, 6-month mobility to Japan is planned.

The Department Materials and Light is highly international and involves several young researchers, PhD students and post-docs. The project is funded by CNRS, ANR (national research agency) and IUF (Institut Universitaire de France).

Required skills and knowledge

Candidates must have knowledge of solid-state physics, crystallography, materials science and be interested experimental research using spectroscopy (optics or X-rays) and X-ray diffraction. The candidate should be familiar with data analysis and have good knowledge of programing (Python or similar). Applications should include a detailed CV; at least two references (persons likely to be contacted); a one-page cover letter; a one-page summary of the master's thesis; Bachelor's and Master's or engineering school grades).

References:

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4. Tokoro, H.; Ohkoshi, S., Multifunctional Material: Bistable Metal–Cyanide Polymer of Rubidium Manganese Hexacyanoferrate. *Bulletin of the Chemical Society of Japan* **2015,** *88* (2), 227-239.
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9. Guerin, L.; Hebert, J.; Le-Cointe, M.; Adachi, S.; Koshihara, S.; Cailleau, H.; Collet, E., Capturing One-Dimensional Precursors of a Photoinduced Transformation in a Material. *Physical Review Letters* **2010,** *105* (24), 246101.
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