Ultrafast Dynamics of Complex Materials Investigated by Time-Resolved Spectroscopies

People involved: Federico Cilento, Wibke Bronsch, Denny Puntel, Manuel Tuniz, Fulvio Parmigiani

Laboratory: T-ReX Facility at FERMI

e-mail: federico.cilento@elettra.eu

A PhD Project at the T-ReX Laboratory at Elettra-Sincrotrone Trieste is available. T-ReX is the laboratory and facility for table-top time-resolved spectroscopies at FERMI, Elettra, Trieste. Here, we study the relevant properties and functionalities of complex materials by means of time-resolved spectroscopies. The materials that are studied display superconductivity, magnetism, charge or spin density modulations, with trivial or non-trivial topology. In the last few years, we have explored the nematic state of iron-bsed-superconductors [1], the momentum distribution of the non-occupied electronic states in topological insulators [2], the symmetry of polymorphic transition-metal-dichalcogenides [3], the lattice vibrations in WTe_2 [4], the photoinduced phase transition in the charge-density-wave material $NbSe_2$ [5] and the influence of the excitation pathway in the non-equilibrium dynamics of a material that displays simultaneously insulating and metallic properties [6], exploiting a combination of table-top and FEL light sources. Moreover, we are active in the development of novel time-resolved spectroscopies [2,3,7].

As a common ground, we study the properties of matter in a photo-excited state which differs from the equilibrium ground state. The intensity of the excitation determines how far the photo-induced state is with respect to the initial state of matter. Typically, at low excitation densities the excited quasiparticles keep memory of the underlying ground state, while at higher excitation densities, states far from the thermodynamic ground state can be reached. These can be either phases obtained through a photo-induced phase transition, or novel states of matter that have no counterpart at equilibrium. Despite the apparent complication, the study of matter in out-of-equilibrium conditions can provide information about the material under scrutiny that, by working at equilibrium, would be much more complex to extract. Examples are the estimation of the electron-phonon coupling constant, or the study of phonons in solids; but this fact applies to many other quantities. And clearly, the use of the non-equilibrium approach paves the way to the control of the properties of matter at ultrafast speeds.

The out-of-equilibrium approach can be applied to a wide variety of spectroscopies, including photoemission (and ARPES), optical spectroscopy, Raman spectroscopy, THz-time domain spectroscopy, and many others. The key is to replace the conventional light source by a source of ultrashort photon pulses, which is a laser. Thanks to the use of such pulses, that can easily be as short as a few femtoseconds (10^{-15} s), it becomes possible to sample the state (and its evolution) of a material with an 'exposure time' of the order of the pulse duration itself. Hence, this is equivalent to take a picture of the sample state with an exposure time of a few femtoseconds, which is something not possible, at present, by means of electronic devices. Only optics can be used to achieve such short timescales. Briefly, the laser output, composed of a train of ultrashort pulses, is divided in two arms, which recombine at the sample: one, called *pump*, induces an impulsive, ultrafast perturbation to the sample, altering its properties. The second one, called *probe*, senses the effect of the excitation on the material's properties. It is the probe that determines the actual spectroscopy used. In our laboratory, we have a number of laser sources and non-linear optical devices to seed both photoelectron and optical spectroscopies. While for photoemission we produce narrowband, ultraviolet pulses with photon energy larger than 6 eV, for optical spectroscopies we generate broadband pulses of white-light (supercontinuum) spanning the infrared and visible spectral range, with which we measure the non-equilibrium dielectric function of samples.

The possible topics of a PhD project at T-ReX comprise both the development of innovative ultrafast photon sources and the use of time-resolved optical and photoelectron spectroscopies for the study of the functional

properties of complex materials. In particular, T-ReX hosts novel photon sources delivering ultrashort (100 fs) photon pulses in the Vacuum-Ultra-Violet (VUV) and Extreme-Ultra-Violet (EUV) spectral regions, seeded by ultrafast table-top laser sources, and devoted to time-resolved photoemission experiments. The use and optimization of such sources will provide the candidate with a deep knowledge and expertise about nonlinear optical phenomena.

Overall, T-ReX hosts three complementary sources of ultraviolet photons, delivering photon energies of 6, 11 and 17-33 eV, for the study of the out-of-equilibrium femtosecond electron dynamics measured by Time&Angle Resolved PhotoElectron Spectroscopy (TR-ARPES) [8] of complex materials. In addition, the Laboratory hosts advanced time-resolved optical spectroscopies for the analysis of the non-equilibrium optical properties of solid state materials.

These advanced spectroscopies pave the way to a number of novel experiments that will be the core of the PhD project. In particular, the sources were designed for TR-ARPES studies with high energy and momentum resolution, high signal statistics and low space charge, allowing to explore the entire Fermi surface of correlated materials. The scientific themes that will be covered during the proposed PhD project will strongly benefit from these novel sources. The common thread of the proposed investigations concerns the study of materials with strong electronic correlations and complex (anisotropic) Fermi surfaces. Electrons occupying different regions of the Fermi surface brings complementary information about ordered phases (for example charge density wave, superconductivity), competing phenomena (for example superconducting gap and pseudogap) or a different degree of electronic correlation (the so-called 'Selected Mottness'). Hence, high-resolution TR-ARPES at large momenta is the best suited technique in order to tackle these themes: i) on the one side, momentum resolution allows to disentangle phenomena localized at precise momentum regions; ii) the non-equilibrium approach allows decoupling ordered phases or degrees of freedom that at equilibrium coexist on similar energy scales. Thanks to the non-equilibrium approach, the ground state of the material can be manipulated and photoinduced phase transitions between ordered phases can be triggered. The focus of the project will be the study of the interplay among these ordered phases connected through photoinduced phase transitions, in order to determine their mutual interactions (competing, coexisting, …) by their non-equilibrium dynamics.

In more detail, the topics that, upon discussion and agreement with the candidate, can be tackled during the PhD project are outlined below. Other topics will likely be explored, depending on the evolution of the scientific community and the availability of new materials in the next few years.

- **Studies of cuprate superconductors**

In the field of copper-based high critical temperature superconductors, a large number of fundamental issues are left opened, despite the intense efforts of the past >30 years. The non-equilibrium approach and in particular Time-Resolved ARPES are specifically best-suited to tackle the following open issues: i) the understanding of the interplay between the (d-wave) superconducting gap and the pseudogap phase (having its fingerprint localized in the antinodal region of the Brillouin zone [9]); ii) the interplay between superconductivity and charge density wave in cuprates (the signature of the charge density wave is thought to be hidden at the 'hot spots' of the Fermi arc [10]). These issues will take advantage of the possibility of photoinducing phase transitions between the superconducting state to the pseudogap state and by the possibility to melt the charge-density-wave order, as allowed by the pump-probe technique.

- **Studies of Alkali-metal-doped fullerenes**

Very recently alkali-metal-doped fullerenes, well known for they can sustain superconductivity up to ≈40 K, have been brought back to the attention of the physics community after the discovery of a possible light-induced superconducting state far above their critical temperature [11], after strong infrared irradiation. However, this finding is highly controversial and debated [12]. In order to try to shed light in this field, the idea is to use TR-ARPES to directly measure the light-induced modification of the electronic states at the Fermi level, where superconductivity manifests with the opening of the superconducting gap. Very briefly, the debate about the development of this 'more metallic' photoinduced state sees on one side the idea that it is

induced by a coherent and resonant optical excitation of molecular vibrations, that enhance the conductivity. On the other side, arguing that the phenomenon is observed in a broad pumping frequency range that coincides with the mid-infrared electronic absorption peak still of unclear origin, a different mechanism was proposed. Since the broad absorption peak represents a "super-exciton" involving the promotion of one electron from the t_{1u} half-filled state to a higher-energy empty t_{1g} state, the IR-induced excitons could act as a sort of cooling mechanism that permits transient superconducting signals to persist up to temperatures much larger than T_C. TR-ARPES can contribute to this debate, by measuring directly the nature of the photoinduced metallic state at the Fermi level.

- **Studies of iron-based superconductors**

Iron-based superconductors have a Fermi surface composed by all the 5 Iron d-orbitals [13,14]. All these electronic states become gapped in the superconducting state, and the natural question is whether the superconducting transition is driven by a conventional BCS mechanism or it is driven by electronic correlations. It was predicted that the hole- or electron-states at the Fermi surface have a different degree of electronic correlation, also termed 'Selective Mottness' [15], that can point toward a purely electronic mediated coupling. This model will be analyzed by TR-ARPES experiments, that can directly measure the correlation strength of each orbital thanks to the measurement of its single-particle lifetime, and also how the photo-induced superconducting-to-metal phase transition is affecting the multiple gaps at the Fermi level. This work will be performed in collaboration with SISSA, where researchers are performing calculations about the 'Selective Mottness' and will provide theoretical support to interpret results by TR-ARPES [16,17].

- **Studies of the excitons in transition-metal-dichalcogenides**

The study of the electronic and optical properties of TMDC [18] far from thee equilibrium is intriguing because the response to photoexcitation is dominated by the formation of excitons, bound states between an electron and a hole, which are particularly effective in few layer samples. We intend to investigate ultrafast carrier dynamics in TMDC and to explore their exciton physics by means of TR-OS, ARPES, and time and wavelength resolved photoluminescence (PL) spectroscopy to gain complementary information. Next, we intend to upgrade our PL setup to perform ultrafast PL spectroscopy and "pump-probe" PL. This upgrade will enable a new option to investigate bright and dark excitons in TMDC. The research will be tailored in order to emphasize the possible technological applications, like light-emitting devices, ultrafast and ultrasensitive light detectors in the UV to THz frequency ranges, and photovoltaic devices.

References

[1] L. Fanfarillo et al., J. Electr. Spectrosc. Relat. Phenom. 250, 147090 (2021)
[2] S. Peli et al., J. Electr. Spectrosc. Relat. Phenom. 243, 146978 (2020)
[3] M. Perlangeli et al., Optics Express 28, 8819 (2020)
[4] D. Soranzio et al., Phys. Rev. Research 1, 032033(R) (2019)
[5] D. T. Payne et al., https://arxiv.org/abs/2010.09826 (2020)
[6] W. Bronsch et al., Faraday Discussions, https://pubs.rsc.org/en/content/articlelanding/2022/fd/d2fd00019a
[7] R. Cucini et al., Structural Dynamics 7, 014303 (2020)
[8] A. Damascelli et al., Rev. Mod. Phys. **75**, 473 (2003)
[9] T. Yoshida, arXiv:1208.2903 (2012)
[10] R. Comin et al., Science **343**, 390-392 (2014)
[11] M. Mitrano et al., Nature **530**, 461 (2016)
[12] A. Nava et al., arXiv:1704.05613 (2017)
[13] G. Stewart, Rev. Mod. Phys. 83, 1589 (2011)
[14] D. Johnston, Adv. Phys. 59, 803 (2012)
[15] L. de' Medici et al., Phys. Rev. Lett. **112**, 177001 (2014)
[16] L. Fanfarillo et al., Phys. Rev. B **94**, 155138 (2016)
[17] L. Fanfarillo et al., Phys. Rev. B **95**, 144511 (2017)
[18] S. Manzeli et al., Nature Reviews Materials 2, 17033 (2017)

Contacts

In order to collect more information, you are very welcome to visit the lab's homepage:
www.elettra.trieste.it/labs/t-rex.html
Additionally, you can visit my webpage, where you also find all the contact information:
www.elettra.trieste.it/People/FedericoCilento
Should you have any question, do not hesitate to contact us.