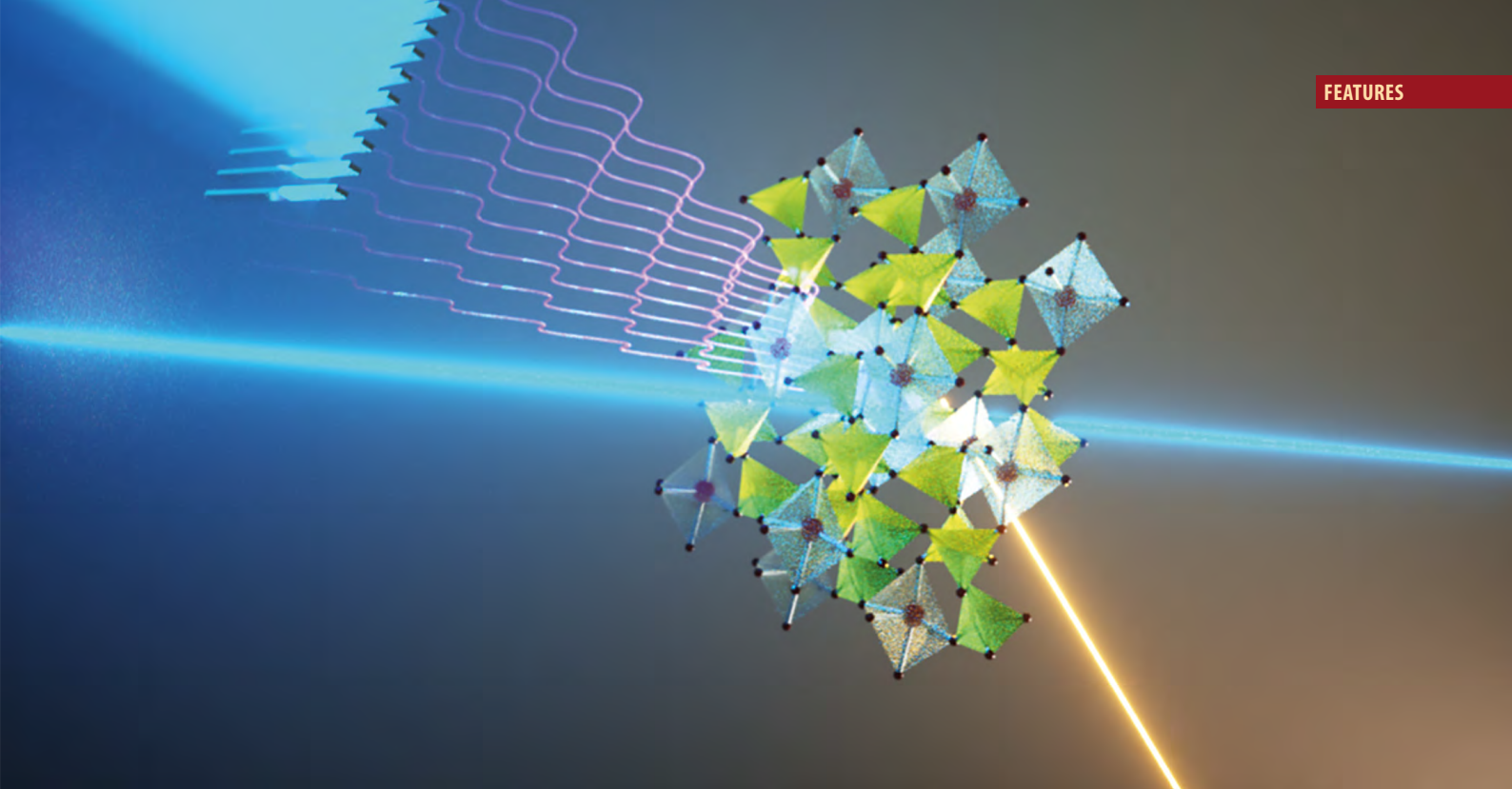




NON-LINEAR X-RAY SCIENCE

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The advent of the laser in the early 1960s represented a revolution in Optics and Spectroscopy that is still impacting our lives to this day. The availability of coherent and intense beams of laser light enabled the birth of non-linear optics as first demonstrated by the historic experiments in 1961 on second harmonic generation, and the first observation of two-photon absorption. The rapid discovery of diverse non-linear (NL) optical methods had a deep impact in Science that were recognised by Physics (1981, 2018) and Chemistry (1999) Nobel Prizes.

These developments were mainly undertaken in the optical-domain (ultraviolet, visible, infrared and terahertz), and led to the birth of photonics and optoelectronics, along with a myriad of new analytical and imaging techniques. [1] On the fundamental side, NL methods have boosted the spectroscopic study of atomic, molecular and condensed matter systems, but also of surfaces and interfaces, such as those exploiting the second-order susceptibility of the material, namely second harmonic generation and sum/difference frequency generation that are operative in non-centrosymmetric systems

(Figure 1). In centrosymmetric systems, the third-order susceptibility becomes the lowest-order non-linearity, leading to phenomena such as third-harmonic generation and the so-called four-wave mixing techniques. These further enhance the above capabilities and allow, *e.g.*, via transient grating spectroscopy, to probe transport phenomena (heat, charge, magnetism, *etc.*) in materials and solutions.

With the femtosecond (fs) and attosecond (as) durations reached by pulsed laser sources, NL methods have benefited from the higher and higher peak powers for driving NL phenomena.

In the past 10-15 years, the advent of Free Electron Lasers (FEL) providing intense, coherent, and ultrashort pulses of short-wavelength radiation in the extreme-ultra-violet (≥ 10 eV, EUV) to the hard X-ray (≤ 20 keV) range, brought several orders of magnitude increase in photon flux per pulse (typ, 10^6) compared to the most commonly used X-ray sources that are synchrotrons, along with ultrashort (fs and as) pulse durations. This made FELs game changers for time-resolved EUV/X-ray spectroscopy and scattering methods. [2] Most significant, they are enabling the non-linear revolution in EUV/X-ray science, just as what occurred in the optical-domain lasers with the 1960s. The field of non-linear X-ray science is nascent, but the past ten to fifteen years have already brought a handful of results. The first FEL was FLASH at DESY (Hamburg, Germany) in 2005, which operates in the EUV to soft X-ray range. The first hard X-ray FEL, the Linac Coherent Light Source (LCLS), was launched in 2009 in Stanford, soon followed by the EUV/soft X-ray FEL FERMI in Italy (Trieste) and the hard XFEL SACLA in Hyogo (Japan). In 2017, three additional hard and soft XFELs went into operation: SwissFEL (Paul Scherrer Institut, Switzerland), European XFEL (Germany) and the Pohang Accelerator lab PAL (South Korea) XFEL.

It can be said that almost all the basic non-linear methods have been demonstrated in the EUV/X-ray range, as recently reviewed. [3] Two-photon absorption (TPA) accesses partially or fully dipole-forbidden transitions, thus complementing information to that obtained using one-photon X-ray absorption. The first TPA studies were carried out in the EUV and in the soft X-ray regime on rare gas atoms, and the cross-sections were found to be 2-3 orders of magnitude larger than theoretically predicted and were attributed to contributions from near-resonant states. They were followed by reports on

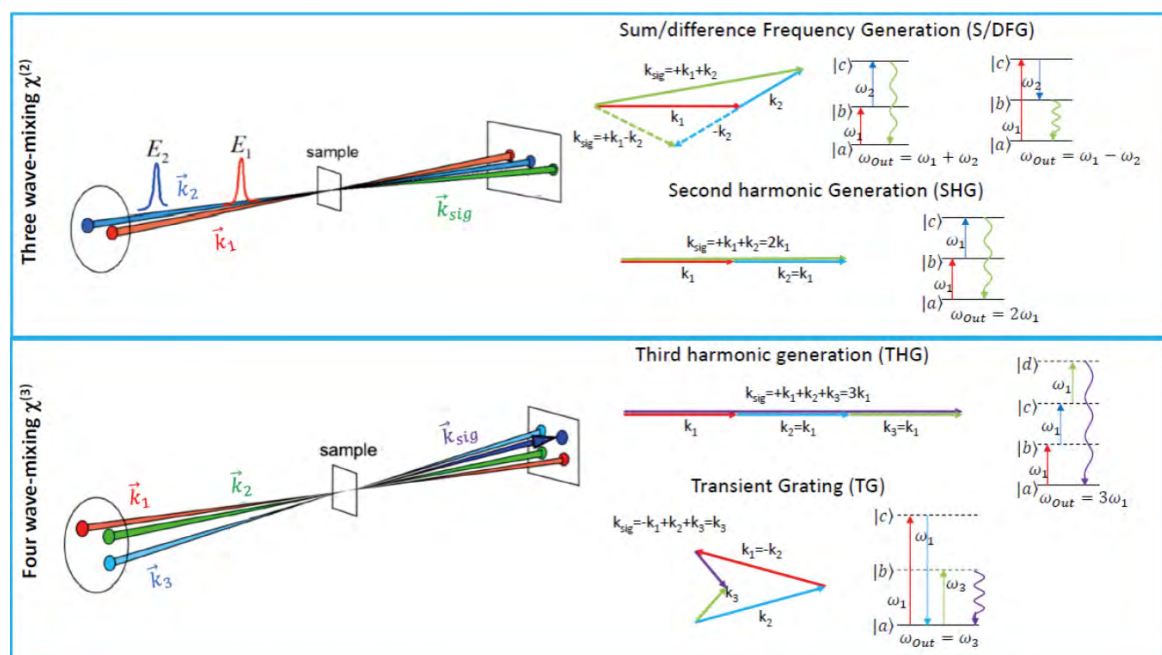
hard X-ray TPA in Germanium and later, in Zirconium, Iron and Copper foils.

Stimulated X-ray emission (XES) and X-ray Raman (XRS) spectroscopy provide information about the energy and dispersion of the elementary low-energy excitations (vibronic, charge, magnon and orbital excitations). Stimulated EUV emission from a single X-ray fluorescence line in a Neon gas was achieved, followed by demonstrations on different solids. In the hard X-ray regime, stimulated XES was demonstrated on copper. $K\alpha$, $K\beta$ emission carry information about the electronic and spin structure of the system, while K_{VIC} (valence-to-core) additionally contains exquisite fingerprints of the chemical bond of the atom with its neighbours, and its oxidation state, covalency, *etc.* By externally stimulating these transitions, the sensitivity of emission experiments, which are inherently weak, was significantly enhanced (by $> 10^5$ over the conventional $K\beta$ emission).

Resonant inelastic X-ray scattering (RIXS) is an ideal tool for populating electronic valence states that are inaccessible at optical wavelengths. Stimulated RIXS (SRIXS) was first achieved for atoms, and more recently in diatomic molecules such as CO or NO. The use of attosecond X-ray pulses was shown to induce electronic population transfer via SRIXS exploiting their broad spectral bandwidth. Both stimulated resonant elastic (SREXS) and inelastic (SRIXS) X-ray scattering were recently reported near the cobalt L3 edge in solid Co/Pd multilayer samples, with 4 to 5 orders of magnitude enhancement over the spontaneous RIXS signal.

In the X-ray domain, sum- and difference-frequency generation (S/DFG) are akin to optically-modulated X-ray diffraction in which X-rays inelastically scatter from optically induced charge oscillations and therefore, they probe optically polarised charge. This additionally

► FIG. 1: A sample of non-linear optical methods based on the second (top) and third (bottom) order susceptibility

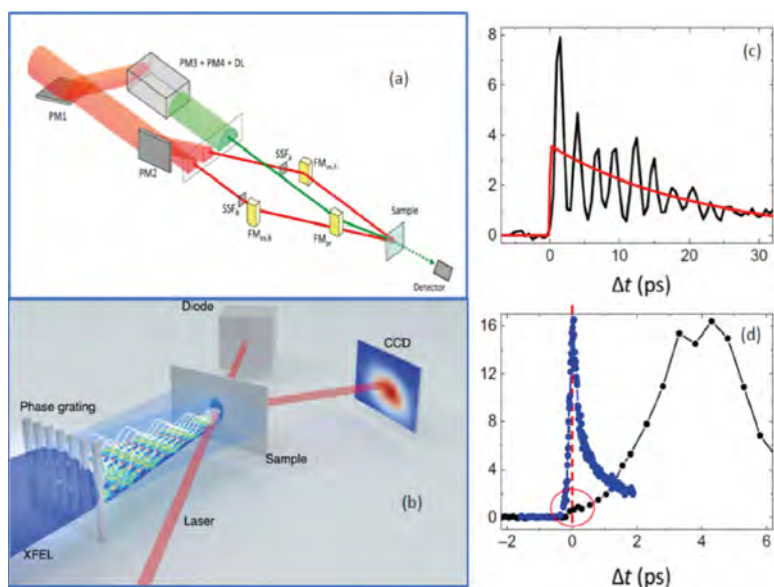


allows the optically-induced microscopic field to be determined as it is closely related to the induced charge. The experimental verification was achieved at XFELs combining an optical with a hard X-ray pulse.

In addition to being interface- and element-specific, S/DFG and second harmonic generation (SHG) can be enhanced by resonance of the relevant photon energies with valence and/or core-level transitions. Extending SHG into the EUV/X-ray domain offers the additional advantage of element-selectivity. There are some important differences with the optical-domain in that non-linearities may be observed in centrosymmetric materials, provided a non-uniform electron density is present. These techniques also allow the monitoring of buried interfaces, in-operando catalytic processes and interfacial electron transfer, to name a few.

Among the Four-wave mixing methods, Transient Grating (TG) spectroscopy is one of the most popular. It consists in crossing two identical incident beams on the sample, where they interfere and produce a grating of excitation (thermal, charges, magnetic, *etc.*) at $t=0$. The decay of the grating by relaxation, diffusion or other processes, is then monitored by diffracting a third, probe beam on the grating (Figure 2). The grating period is determined by the wavelength and crossing angle of the two incident beams. Going from the visible to the hard X-ray range decreases it from microns to nanometers. This offers a unique approach to access the meso to nanoscopic range of transport phenomena. This is of particular interest as with the miniaturization of optoelectronic devices, nanoscale transport phenomena need to be understood and described, and specifically the changes from ballistic to diffusive transport. The first demonstration of EUV-TG was achieved in 2015 and it used an optical probe pulse. The advantage of mesoscale periods is however cancelled by the use of optical probe pulses, therefore this first achievement was followed by an all-EUV TG experiment (Figure 2a). [4] More recently, demonstration of hard X-ray TG was achieved exploiting the Talbot effect (Figure 2b), with promising perspectives to monitor nanoscale transport, especially when all hard X-ray TG will be demonstrated.

The above account gives a very succinct presentation of the capabilities and achievements in non-linear EUV/X-ray science. Considering the diversity and flexibility of non-linear optics, these breakthrough experiments are heralding the birth of a new era. Just as in the optical regime, non-linear EUV/X-ray science promises highly diverse and versatile applications in the study of interfaces/surfaces, transport phenomena, optoelectronics, *etc.* While all the above-mentioned methods have a high potential for applications, the holy grail is to reach core-level multidimensional spectroscopy, [5] which will allow detecting the cross-talk between atoms in any type of system. ■



About the Authors



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The authors are leading figures in X-ray science. MB is known for his contributions to non-linear X-ray science, MC is a pioneer in ultrafast X-ray spectroscopy, CM has been a major driver of NL EUV science and CS is the key architect of its extension into the hard X-ray regime. MC is founder and former director of the Lausanne Centre for Ultrafast Science (LACUS) and CM is director of the FERMI FEL.

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▲ FIG. 2: a) split-and-delay scheme for all EUV TG spectroscopy; b) Talbot effect to create a TG using hard X-rays; c) all EUV-TG signal of Silicon Nitride showing coherent acoustic modes; d) comparison of the EUV-TG signal of Silicon Nitride probed by an EUV pulse (black) and an optical one (blue). This reflects the fact that the refraction index changes at optical wavelengths are sensitive to electronic excitations in the conduction/valence band, while at EUV wavelengths, they are sensitive to changes in the total electronic density, and are dominated by the lattice response.