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WORKSHOP REPORT

Scientific Opportunities with very Hard XFEL Radiation

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Introduction

Access to very hard XFEL radiation energies up to 70-100 keV, well above the currently achievable 30 keV, enables new ways of exploring materials properties and new investigations of a range of scientific questions by powerful XFEL methods.

The key enabling properties of very hard x-ray energies include:

- Larger penetration depth for bulk sensitivity and access to complex sample environments
- Larger momentum transfer at moderate scattering angles for improved accuracy in modelling, for inverse analysis schemes, and for crystallography of small unit cell materials
- Access to core-level spectroscopy of heavier elements and nuclear resonances
- Reduced radiation damage for high repetition rate tracking of induced (pumped) dynamics and stochastic phenomena in heterogeneous samples.

In turn, these properties will provide new solutions for tackling the grand challenges of society. Examples include the UN sustainability goals[1] 7 (Ensure access to affordable, reliable, sustainable and modern energy for all) and 9 (Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation), as well as the EU Green Deal[2] (cleaner energy and cutting-edge clean technological innovation performance; longer lasting products that can be repaired, recycled and re-used; globally competitive and resilient industries *e.g.* for green energy). An important path to reach these goals goes via the creation of advanced materials and devices

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[1] https://sdgs.un.org/goals

[2] https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en

with new and improved functionality, including by computational design, by reducing the energy consumed during fabrication and operation of such materials and devices, and by further ensuring sustainability in the development of new materials based on earth-abundant and non-toxic constituents.

To explore this potential, an international workshop was convened to bring together leading expert scientists and emerging science leaders/young researchers, to push forward their ideas and discuss scientific opportunities and novel techniques that can leverage very hard XFEL radiation. The aim of the workshop "Scientific opportunities with very hard XFEL radiation” (https://indico.desy.de/event/33463/) was to identify scientific questions and applications requiring very hard XFEL radiation (> 40 keV) in the context of the strategic directions that are being currently discussed at the European XFEL for major upgrades of its instrumentation. The event was attended by 114 in-person participants from 16 countries. It was organized in five plenary sessions, selected by the scientific program committee:

- Applied Materials and Industrial Applications (Chairs: K. Saksl and S. Pascarelli)
- Structural Dynamics in Disordered Materials (Chairs: F. Bertolotti, I. Robinson)
- Dynamics of Functional Materials (Chairs: A. Dippel, M. Meedom Nielsen)
- Enabling Techniques and Instrumentation for New Scientific Avenues (Chairs: D. Dye, A. Madsen)
- High Pressure, Planetary Science and Geology, Electron Dynamics, Warm Dense Matter, Relativistic Laser Plasma, Strong Field Science (Chairs: A. Benuzzi-Mounaix, S. Pikuz, U. Zastrau)

The reports below summarize the presentations and some of the discussions of the five sessions.

Contents

1 Applied Materials and Industrial Applications

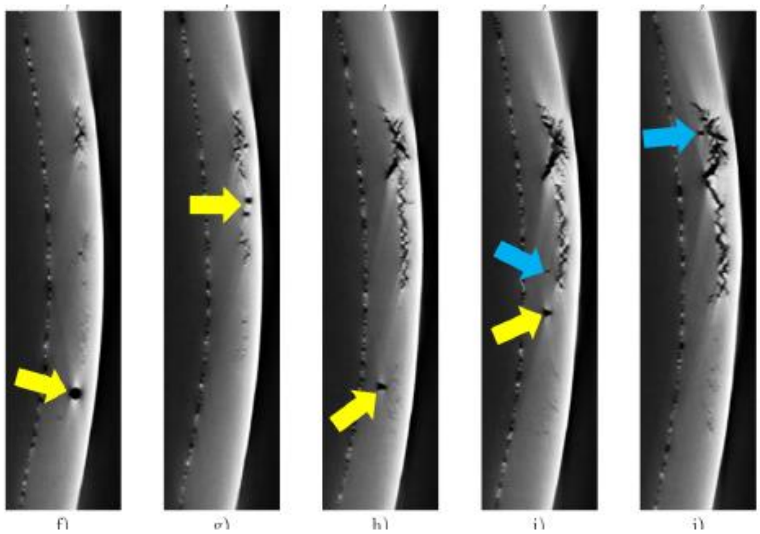
Session Chairs: Karl Saksl (Slovak Academy of Sciences), Sakura Pascarelli (European XFEL)

The opening session of the workshop addressed very diverse applications in areas of applied materials and processes of interest for industry. The talks presented pressing questions related to development of more sustainable, longer lifetime materials, better and more efficient catalysts for cleaner energy production, better real time control of irreversible processes relevant to additive manufacturing, inertial fusion or in hierarchically organized materials.

In the first talk of the session, Laurent Berthe (PIMM and CNRS, FR) presented perspectives for materials under laser-induced shock and under extreme conditions (I.1-I.3). He explained that the lack of diagnostics with sufficient bulk sensitivity, spatial and temporal resolution is hampering development of technology in two important rapidly evolving areas: 1) planetary security and materials for spacecraft protection shields against debris and 2) design and manufacture of more sustainable, lighter, and longer lifetime materials and structures.

For the former, it is necessary to understand the structural changes induced by High Velocity Impacts (HVI) (i.e. 7-30 km/s) in materials, at the nano, micro and meso scales and at the relevant timescales. The range of materials is wide, and spans from polycrystalline metals including relatively novel high entropy alloys, metallic glasses, silicon, composites, polymers, ceramics, powder/sand and rocks. Shocks induced by laser plasma reproduce pressure loadings involved in such impacts, which may reach 100 GPa in 100 ns. Codes to model the underlying physical processes exist but experimental data is required for their validation. Ultimately, the objective is to design new technologies to improve projectile-target coupling and discover innovative materials and geometries for structural protection. Processes to be studied are laser ablation, shock wave propagation, crater formation, phase transformations, but also investigation of the cloud of debris, including its generation, flight, particle size, phase change, impact on surface, and reactivity with atmosphere.

Figure I.1 *Observing dynamic damage at grain size resolution. Figure from reference I.4.*



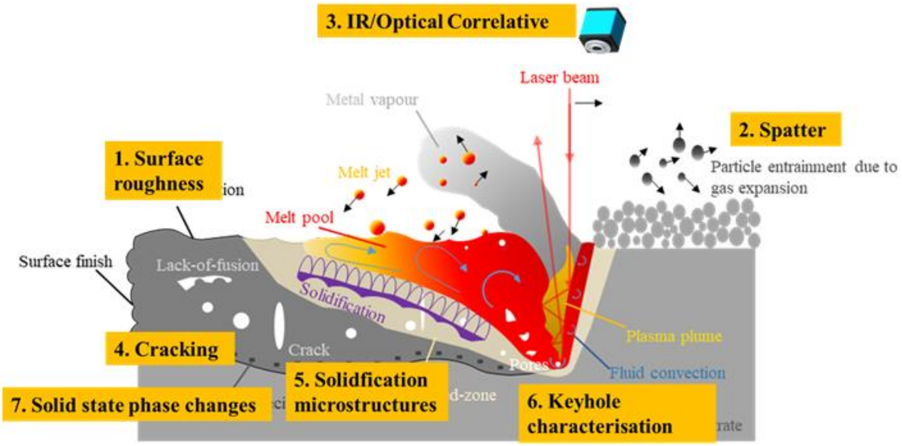
For the latter, it is necessary to develop new time and space resolved diagnostics to measure residual stress fields and to observe delamination and fissure propagation in materials such as carbon fiber-reinforced polymers and metals. One of the most pressing goals is to create digital twins for Laser Shock Peening and life time prognostic for Structural Health Monitoring (SHM) respectively. Today, *in-situ* diagnostics focus on visible imaging and velocimetry to investigate residual impact on materials (crater and bulk material) and recovered debris. What is instead required is time (ps to µs) and space (nm to mm) resolved hard X-ray diagnostics to observe shock wave propagation in a volume of the order of the mm^3 of material, to observe crater formation at depth of the order of the mm, to measure densities at µm/ns scales and the velocity of debris, to detect phase changes/chemical synthesis at grain scale in bulk and in debris, and to study secondary impacts of debris on surface (solid or/and covered by particle) and clouds collision.

In the second presentation, Andreas Stierle (DESY and University Hamburg, DE) addressed outstanding questions in heterogeneous catalysis processes, which govern most of the chemical production, energy conversion and exhaust cleaning operations. Many important reactions have low turn-over frequencies, catalysts are inefficient, and a better understanding and tailoring of reaction pathways is of huge importance for the most urgent problems on earth, such as energy production, conversion and storage, CO_2 activation and air purification. Open questions are related to the mechanisms of bond breaking/making during a catalytic reaction, the identification of intermediate short-lived states, the influence/role of the support (static/dynamic picture), the nature and role of spatio-temporal thermodynamic fluctuations, nanoparticle shape changes under thermodynamic equilibrium conditions, fast kinetic processes (gas induced), and tailoring of mechanisms at ultrafast time scales (down to the femtosecond). Reaction pathways are predicted by theory combined with ultra-fast optical spectroscopy but structural fingerprints at ultrafast timescales are lacking. The availability of very hard XFEL radiation as an in-situ probe to track atomic positions at ultrafast time scales during a catalytic reaction would allow identification of reaction pathways and structural intermediates. Hard X-rays allow much more effective reciprocal space mapping from surfaces and nanoparticles in stationary geometry, making surface structure changes during catalytic reactions accessible. Especially for the case of nanoparticles dynamical shape changes, providing more active reaction sites may be detected. In-operando studies are pursued at high energy synchrotrons, such as PETRA III and ESRF in Europe, with excellent results down to the millisecond timescale using hard x-ray photons. But accessing the sub-ns timescale to address the above questions requires both the ultra-short (femtosecond) pulses of XFEL radiation, and significantly higher photon energies than available at XFELs today. In the 50-80 keV photon energy regime nanoparticle ensembles give rise to stationary surface sensitive diffraction signals, which make the experiments feasible at all, since no angular scanning is required. Investigation of surfaces or nano-particles ensembles under photo induced methanol synthesis would be a first flagship experiment, impossible to address today.

In the third talk, Peter Lee (University College London, UK) focused on the challenges encountered in the optimization of additive manufacturing (AM), the process of creating an object by building it one layer at a time. AM is transforming production in many industrial areas, but in particular in the medical, energy, aerospace, consumer products and transportation industries. His talk focused on the needs for better real time control of processes involved in AM, such as melting and solidification to overcome distortions, defects and cracking that lead to failure, for example because of strain and porosity. During AM, materials interaction is so fast that available knowledge (i.e. from casting) does not apply anymore; heating and cooling rates are a million times larger than with traditional casting. Today there is a severe lack in understanding the underlying physics that governs these processes, characterized by the formation of highly non-equilibrium microstructures and speed of sound transformations (down to ns).

This is why ultra-high speed probes, combined to the high penetration power of hard X-rays to probe deep within opaque specimens, are needed so much. Imaging at high energy synchrotrons (I.6, I.7) is providing new insights into additive manufacturing but the flux is not sufficient to simultaneously address the relevant timescales and relevant spatial resolution. Both are required to capture the detail of fluctuations, dynamics of plasma formation, microstructure and composition change. Most of the applications are using Al, but the aim is to also address the 3d metals Ti, Ni and Cu, which are of paramount importance in many technological applications. Examples of unanswered questions are keyhole stability, oscillation and pore formation, particle and pore motion, coalescence and capture, pore cracking mechanisms, including transgranular liquation cracking (superalloys to magma, and silicon wafers…), high temperature diffusionless transformations and nano-scale phase formation. The time scales of the mechanisms controlling these phenomena are ~ ps and new methods are needed to understand the underlying physics.

Figure. I.2 *Schematic illustration of major phenomena in Laser Plasma Bed Fusion (LPBF), one of the most well-known Additive Manufacturing processes. Figure from reference I.5.*



In the fourth presentation Hugo Doyle (First Light Fusion, UK, ‘FLF’) discussed perspectives of using hard X-ray FEL radiation to better diagnose performance of projectile fusion, a new approach to inertial fusion that is simpler, more energy efficient, and has lower physical risk3,4. Recent confirmation of net energy gain via indirectly driven inertial confinement at the National Ignition Facility (NIF) has renewed private and government interest in this field of research. Previous research on projectile fusion indicated very high velocities are required to induce fusion ignition. FLF uses hydrodynamic pressure amplification to reduce the required projectile velocity, that is, the implosion velocity imparted into the fuel is much faster than the original impact. The amplifier is also used to create convergence. Whilst the initial impact comes from only one side, the amplifier output compresses the fuel spherically. This is crucial for reaching the required final density. It is critical to the development of this amplifier technology that FLF can accurately diagnose performance and high-energy XFEL radiation could substantially extend existing capabilities. In the process, a projectile impacts a target containing a high-Z metal capsule filled with fuel. The target must focus the

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[3] https://firstlightfusion.com/technology/power-plant

[4] https://www.nature.com/immersive/d41586-021-03401-w/index.html

energy of the projectile, imploding the fuel to the temperatures and densities needed to make it fuse. In order to increase efficiency, it is necessary to understand and ultimately predictively model the processes that occur inside the capsule. X-ray imaging at high energy synchrotrons is currently utilized to retrieve density modifications, with sufficient contrast, of the projectile-target interaction region inside the capsule. Data on the incident shock, rarefaction waves, and jetting is then compared to hydrodynamic simulations. The talk discussed the limitations of this approach, essentially demonstrating that imaging the pressure release into fuel, and in particular the fine details of the associated rapid fuel instabilities, requires spatial (< µm) and time (< µs) resolutions not available today. The investigation of the compressed fuel in a realistic environment (i.e. the capsule), in particular in the Warm Dense Matter regime, requires novel ultrafast methods that are sensitive to temperature and density. At XFELs, X-ray phase contrast imaging and inelastic X-ray scattering are being utilized to retrieve the macroscopic density (the former) and the free-electron density, temperature and ionisation state (the latter) in shock-driven solid-density targets. These constrain the Equation of State and validate modelling. However, up to now, these investigations are limited to model systems because the XFEL X-ray energy is not sufficiently high for *in-situ* investigation of ‘large’ and uniform conditions. Overall, there is a desire to study material in the Warm Dense Matter and High Energy Density regimes with increased accuracy, resolution and transmission [I.8]. Such measurement accuracies are achievable with X-rays of sufficiently high energy to penetrate the high-density material. These applications also call for high repetition rates (MHz, or even pulses at GHz repetition rate) to allow sequential probing during a single ‘shot’ of the driver (a laser, a gas gun or a pulsed power device).

In the last presentation, Friis Henning Poulsen (Danish Technical University, DK) addressed challenges in the investigation of irreversible processes within realistic environments in hierarchically organized materials: plastic deformation or martensitic phase transformation in metals, switching of domains in ferroelectrics, flux lattices in superconductors, biomineralization in bones, flow in geomaterials, 3D printing. The scientific challenges here are to understand the physical mechanisms underlying the patterning, and to predict the strength of the material from first principles. This would enable materials design by computing. Hierarchically organized materials must be probed on all time and length scales [I.9]. For example, structural characterization in metals needs to address the length scale of grains (~ 100 µm), subgrains (~ 1 µm), dislocation boundaries (~ 100 nm), dislocation (~ 10 nm) and down to the atomic structure. Devices (such as batteries or fuel cells) are also multiscale objects. Optimization of a device requires being able to relate how structural modifications at all length scales relate to changes in performance. Dynamics at these different length scales are dominated by irreversible and stochastic processes, which implies that the time resolved characterization must rely on individual frames with sufficient S/N ratio (single movie mode). Multiscale 3D X-ray microscopes have been developed at synchrotron radiation sources and these have been employed to follow processes down to the 100 ms timescale below which single movie mode becomes flux limited. First pilot projects at XFELs employing Dark Field X-ray Microscopy (DFXM) have succeeded in extending the accessible timescale down to the microsecond for irreversible processes, and down to the picosecond for reversible processes. Phonons in diamond launched by an optical laser-induced strain wave have been photographed in real time using a pump-probe scheme (LCLS and PAL FEL) [I.10].

Four of the areas of application listed above were specifically covered, each addressing different materials and processes: plastic deformation, martensitic phase transformations, ferroelectrics and power electronics, flux lattices in superconductors. All require hard (> 40 keV) XFEL radiation, in order to obtain bulk information (the former two applications) or penetrate realistic environments (the latter two applications).

Speakers and Titles:

- Laurent Berthe (Process and Engineering in Mechanics and Materials laboratory (PIMM) and CNRS, France)
  Perspectives for materials under shock induced by laser processes and materials under extreme conditions

- Andreas Stierle (Centre for X-Ray and Nanoscience CXNS, DESY and University of Hamburg, Germany
  Time Resolved High Energy X-ray Diffraction from Nanostructures and Interfaces
- Peter Lee (University College London, UK)
  Is hard XFEL needed to image additive manufacturing processes in real and reciprocal space?
- Hugo Doyle (First Light Fusion, Oxford, UK)
  Applications for Very Hard XFEL Radiation at First Light Fusion
- Henning Friis Poulsen (Technical University of Denmark)
  Multiscale materials science: movies of irreversible processes within realistic environments

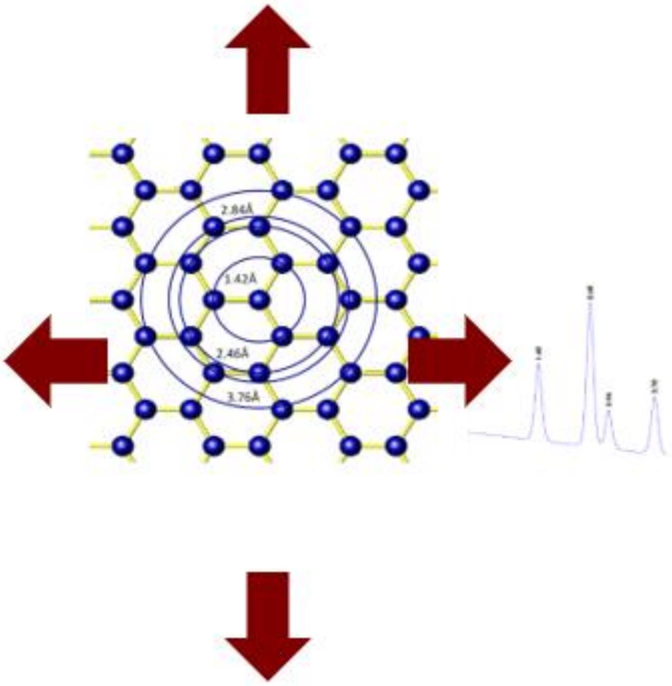
2 Structural Dynamics in Disordered Materials in Real and Reciprocal Space

Session Chairs: Federica Bertolotti (Uni Insubria, IT) and Ian Robinson (UCL, UK)

In this session, several speakers made the case for high-energy photons to increase Q_{max} (the maximum available Q, where $Q = 4\pi \sin\theta/\lambda$, the magnitude of the scattering vector), which is particularly critical for Pair Distribution Function (PDF) applications. Moreover, the use of high-energy photons will increase the penetration depth of the X-ray beam and reduce the sample damage and X-ray beam absorption effects. While the X-ray signal can be recorded for such thick samples in femtosecond exposures, it is a challenge to couple the femtosecond pumping laser to the entire sample in order to achieve picosecond pump-probe information about local structure.

In their introductory talks, David Keen (ISIS Neutron and Muon Facility, UK) and Simon Billinge (Columbia University, NY, US) both made the case for ultra-fast total scattering (TS) and PDF measurements using hard XFEL beams. X-ray TS and its Fourier transform (PDF) have become the method of choice for determining structural disorder within materials since the advent of high-energy synchrotron X-ray diffractometers. To date, these techniques have not been transferred to XFEL facilities because of their more modest (< 24 keV) beam energies, which limits the accessible Q_{max}. This is slowly changing, and the increase of XFEL energies towards 30 keV is opening the possibilities for ultrafast (*uf*)-TS/PDF measurements with useful, albeit still modest, spatial resolution. Instrumentation using existing high-energy XFEL beams might be optimised for *uf*-TS/PDF measurements and the following scientific opportunities can be opened once higher-still X-ray energies become available at XFELs. The X-ray energies of choice for PDF measurements at synchrotron sources are 60-100 keV. Any phase transition can be followed *in-situ*, by taking snapshots captured during the change of phases, as well as high-pressure/temperature liquid structures, recrystallizations, gas-separation, molecular transport within porous materials, charge-discharge processes in batteries, and nucleation of nanoparticles. The strongest case for making high-energy X-rays routinely available at the European XFEL is that any flux-limited experiments with *uf*-time resolution on functional materials can be performed to shed light on their structural properties during operational /transformation conditions.

Figure II.1 *The PDF gives a direct measure of how a local bonding state or coordination of an atom is modified through photoexcitation, and how the change propagates from the location where it occurred. Figure from reference II.1.*



The atomic PDF method is growing in popularity as an approach for studying local structure in nanomaterials, amorphous materials, molecular materials, and liquids, as well as a growing interest in the study of local symmetry-breaking in bulk crystals. It is a direct measure of the local structure in the vicinity of an atom. Despite this, to date, there has been very little work in measuring *uf*-PDF. The reasons are technological rather than scientific. First, to get a quantitatively reliable PDF, high Q_{max} values (>20 Å^{-1}) are required, which requires good fluxes of short wavelength x-rays (> 40 keV when using 2D detectors in transmission). Second, it is needed to measure this wide range of reciprocal space quantitatively with low backgrounds and a linear detector response. These limitations can now be addressed with the latest generation large area 2D detectors and the future development of hard X-ray FELs. The PDF is a key representation of the structure in the context of time-resolved measurements, because whenever the local bonding state or coordination of an atom is modified through photoexcitation, it gives a direct measure of that change, and how it propagates with time from the location where this occurred. There are no moving parts to the PDF measurement and it is becoming popular in chemistry and materials science with >200 publications a year and 11,000 citations.

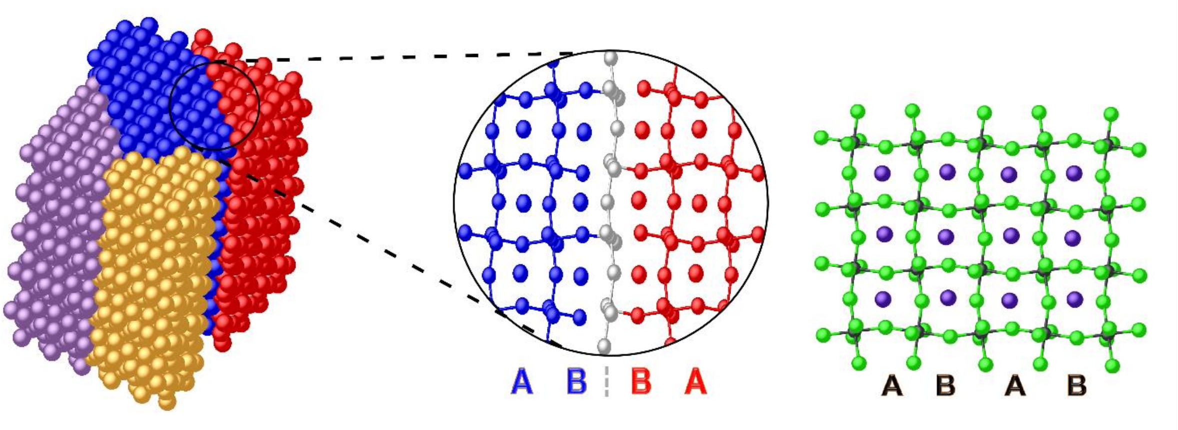
Karen Appel (European XFEL) presented the structure, properties, and phase transitions of silica melts and glasses under *in-situ* conditions within the Earth and rocky planets. Silicate and iron-based compounds are major constituents of terrestrial planets and have a strong impact on planetary evolution and properties. However, information is still scarce on the properties of silica melts under *in-situ* conditions, crucial for understanding the early differentiation events that occurred on Earth and other rocky planets. The main reasons for this are that these melts are not directly accessible and that experiments under *in-situ* conditions are extremely challenging. In addition, their properties change widely with pressure, temperature, and chemical composition thus opening a wide parameter range. Most information on the structure of amorphous silicates is currently obtained with X-ray Raman (XRS) and PDF analysis on SiO_2 glass (or GeO_2, a useful analogue) [II.2, II.3] at room temperature during static compression in a diamond anvil cell (DAC).

An emerging way to study melts under *in-situ* conditions is with optical long-pulse laser dynamic compression techniques that achieve the most extreme pressure-temperature (P-T) states. These extreme states are only very short-lived (on a nanosecond timescale) and nowadays can be probed either with hard synchrotron or XFEL radiation. The short pulse length of the XFEL radiation will give fs-long snapshots of the material while it is excited to extreme temperatures and pressures and the evolution of the sample during dynamic compression can be studied [II.4, II.5]. Most importantly, studies by dynamic compression have the advantage that the sample does not need to be constrained in a sample container (like in DACs) that might mask the signal or react with the sample while the measurement is performed.

However, all published studies that were performed so far at FELs are limited to an accessible Q_{max} of 7 Å^{-1}. Improving this for Earth science applications will result in significantly better models for melt properties and planet evolution, adding key input to long-standing scientific questions, and similarly for studies of glasses of industrial and everyday relevance like mobile phone displays (Panzerglas) or window glasses.

Antonietta Guagliardi (CNR Roma, IT) talked about *uf*-lattice dynamics in lead halide perovskite (LHPs) nanocrystals (NCs) by reciprocal space TS analysis. They are emerging as the next-generation semiconductor materials, strongly impacting photovoltaics and other relevant technological sectors, LHPs [$APbX_3$, A = Cs^+, CH_3NH^{3+} (methylammonium, MA) or $CH(NH_2)^{2+}$, formamidinium, FA; X = Cl^-, Br^-, I^-] have been disruptive in the field of colloidal semiconductor NCs. Bright and narrowband (< 100 meV) photoexcited emission can be easily tuned from the visible to the near-infrared regions, through facile low-temperature synthesis. The atomic-scale origin of the peculiar optical behaviour and the photodynamics of LHPs is currently the focus of intense research. A heavily debated phenomenon is the long lifetime of excitons (in the nanosecond range in NCs) and diffusion lengths. One possible explanation of such a slow hole-electron re-combination rate calls into question the formation and relaxation of large polarons (originating from strong exciton-phonon coupling) on a sub-picosecond timescale [II.6]. *Uf*-time-resolved X-ray total scattering experiments will shed light on this phenomenon by directly observing the related lattice/structural dynamics.

__Figure II.2__ Orthorhombic coherent subdomains in cesium lead halide perovskite nanocrystals. Figure from reference II.7.



With this aim, recent ps-resolved optical pump ultrafast electron diffraction (UED) experiments on fully inorganic and hybrid LHPs NCs have been performed and coupled with total scattering methods of analysis in reciprocal space [II.8]. However, UED has several limitations, associated with the sample environment (dry NCs deposited on a TEM grid, in vacuum) leading to unavoidable preferred orientation effects, electron beam-driven sample damage, and very poor *Q* and angular resolutions. Ideally, these drawbacks will be overcome by implementing pump-probe experiments on semiconductor NCs at XFELs, coupled with high-energy beams, *uf*-time resolution, and flexible sample stages. Efforts in this direction will allow the development of experimental protocols and quantitative analysis tools for characterizing photoexcited out-of-equilibrium transient states and photodynamics in LHP NCs, and ultrasmall quantum dots in general. These are very promising materials for applications in light-emitting devices, solar cells, and quantum technology.

Lennard Krause (Aarhus University, DK) talked about pump–probe single-crystal XFEL experiments for structural determination applied to small-unit-cell systems. X-ray serial crystallography has seen significant progress through XFEL studies [II.9] mainly because the short pulse durations remove effects of beam damage and atomic motion, and because the extreme brilliance reduces the crystallite size required to obtain sufficient scattering intensity.

Recently, a dedicated pipeline for small unit-cell systems has been published [II.10], capable of handling all steps of data reduction from spot harvesting to merged structure factors. It has been successfully implemented to solve the structure of $K_4[Pt_2(P_2O_5H_2)_4]\bullet 2(H_2O)$, as a benchmark case of study. However, there are still challenges that higher energy X-ray beams would solve. The partiality correction critically relies on accurate determination of the crystal orientation, which is complicated by the low number of diffraction spots for small-unit-cell systems. By compressing reciprocal space with higher energies, more diffraction spots will be observed per shot, improving the performance of the orientation refinement and generally making more data available. As of now, the impact of systematic errors such as absorption and extinction on the structure solution/refinement remains buried under the larger errors introduced by the partiality correction and inter-shot scaling. Again, the application of a high-energy XFEL will minimize systematic errors, facilitate a more accurate structural analysis, and will enable investigations of excited states and reaction intermediate chemistry.

Simon Billinge (Columbia University, NY, USA) reported a pilot experiment at LCLS (SLAC) which is a recent attempt to obtain moderate resolution, quantitatively reliable, *uf*-PDFs. They studied Ir dimer dissociation in the thiospinel $CuIr_2S_4$, upon photoexcitation. The PDF analysis in this case highlights the propagation of the local photoinduced dissociation throughout the $CuIr_2S_4$ structure. Despite great efforts to prepare thinly spread, fine powders, only about 20% of the sample was excited by the laser pump. Significant challenges had to be overcome in obtaining reliable data reduction for these measurements, but the difficulties were overcome and quantitatively reliable PDFs were obtained, with good statistics and ps time resolution. The higher real-space resolution measurements available with higher incident X-ray energies from a high energy source, would address a wide range of scientific problems where *uf*-time responses are needed for scientific insights: from sustainable energy through catalysis to pharmaceuticals; earth science; chemistry, and any science involving nanomaterials. A proposal to develop capabilities to do serial nanocrystallography was also discussed.

Crystallographic data would be collected analogous to serial crystallography, but with the goal of reconstructing the 3D-ΔPDF from the randomly oriented diffraction patterns rather than solving a crystal structure. This would open the door to structure solutions and the study of defects in very small objects <10 Å, which is currently an unsolved general problem. Again, a higher real-space resolution is needed to develop these measurements over a wider Q-range with higher energy incident x-rays.

Speakers and Titles:

- Karen Appel (European XFEL)
  Structure, properties and phase transitions of melts and glasses at in-situ conditions within Earth and rocky planets
- David Keen (ISIS Neutron and Muon Facility, UK)
  Ultrafast total scattering pair distribution function measurements using hard XFEL beams
- Antonella Guagliardi (CNR Roma, IT)
  Ultrafast lattice dynamics in halide perovskite nanocrystals by reciprocal space total scattering analysis
- Lennard Krause (Aarhus University, DK)
  Toward pump-probe single crystal XFEL refinements for small-unit-cell systems
- Simon Billinge (Columbia University, NY, USA)
  Ultrafast atomic pair distribution function analysis

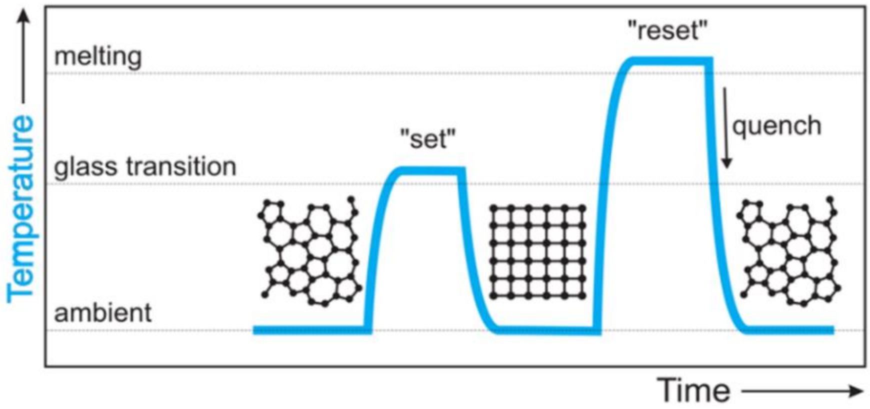
3 Dynamics of Functional Materials

Session Chairs: Ann-Christin Dippel (DESY, DE) and Martin Meedom Nielsen (Danish Technical University, DK)

In this session, five speakers presented talks on functional materials within the areas of information technology, catalysis, magnetic devices and high-strength metallic components. In the broader context, all of these research fields aim to tackle the grand challenges of society.

The session started with two talks on amorphous materials and the structural rearrangements and kinetics of their formation. In the first, Peter Zalden (European XFEL) explained the concept of memory devices using phase change materials as an alternative to the dynamic random-access memory (DRAM) present in practically every computing device today [III.1, III.2]. While the information stored in these DRAM cells needs to be constantly re-written, new non-volatile memory devices have the potential to form the basis for more efficient systems with respect to performance and energy consumption. A phase change material can be stabilized in two states with different electronic or optical properties, like resistivity or refraction, which translate into digital binary information (0 or 1). Typically, the different states occur in the crystalline and the amorphous phase, and switching between these states involves manipulating the material that constitutes the digital bit to either crystallize or to convert into a solid melt within 1 ns. Both transformations are driven by heat that is applied through electrical current to a particular node of a matrix. For the cases of AgIn:(Sb_2Te) and $Ge_{15}Sb_{85}$, the speaker demonstrated that the local atomic structure in the liquid state differs for high and low temperatures. So far, the first and second coordination shells have been described. However, the resolution obtainable in the scattering experiments on the required sub-picosecond time scale is too coarse for analyzing in detail the structure out of equilibrium due to the limited Q space coverage.

__Figure III.1__ The “phase-change” memory cycle. Figure courtesy of P. Zalden.



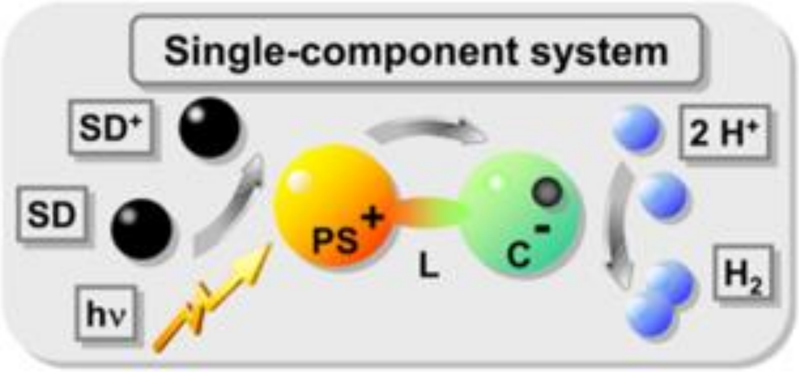
In the second talk, Jerzy Antonowicz (Warsaw University of Technology, PL) focused on metallic glasses made from single elements or alloys [III.3, III.4]. Glassy metals form an emerging class of metallic materials with e.g. exceptional mechanical and magnetic properties that differ substantially from those of their crystalline counterparts. Furthermore, the fabrication conditions for such 'solid liquids' and typical crystalline metals differ significantly. Both processes usually start from the molten state. When the liquid metal cools slowly in equilibrium it adopts the thermodynamically stable crystalline form after falling below the melting point. On the other hand, vitrification requires quenching of the melt, a non-equilibrium cooling that 'freezes' the atoms before they can order into a periodic structure. The kinetics of glass-forming can change over twelve orders of magnitude depending on composition, but the reasons for this are unknown. Clearly, the required quenching rates immensely affect the energy input and the technical challenges of uniform heating and cooling when producing these materials on a large scale. Local superheating effects play an important role in this context. To comprehensively understand the underlying mechanisms, it is essential to follow the changes of occupation in different atomic clusters from the equilibrium melt through the supercooled melt to the glass and compare them with molecular dynamics simulations that predict different mechanisms for different degrees of superheating. Signatures of atomic clusters such as icosahedra have been observed, but the currently limited Q range cannot be used to derive high-resolution structural information in reciprocal space or to access higher order Bragg peaks to determine temperature.

A common theme highlighted in both these presentations, was the need to follow how the atoms are coordinated in the liquid state and during the transition into the solid state. For a melt and an amorphous solid, total scattering and PDF analysis are the most suitable tools to obtain the required information on the atomic short-range order. An XFEL facility that provides ultrashort pulses of high-energy photons will collect high-quality total scattering data with sufficient time resolution to track the atomic rearrangements during solidification into either the amorphous or the crystalline phase. Of particular interest in the study of phase change materials are questions on how the diffusivity, i.e. the inverse of the viscosity, and atomic short- to medium-range order on the one hand and, on the other hand, structure and kinetics during their solidification are linked. In the context of the metallic glasses, the aim is to understand which structural rearrangements cause the slowdown of atomic motions in supercooled metallic liquids and the microscopic origin of the compositional dependence of their glass-forming ability.

In the third talk of the session given by Zahir Islam (Argonne National Laboratory, US), the focus changed from highly disordered matter to single-crystalline correlated-electron materials [III.5, III.6]. The speaker introduced different properties and functions of high-temperature superconductors including zero-electrical resistance, magnetostriction and piezomagnetism. Competing order phenomena, such as charge density wave vs. time-reversal symmetry, are known to exist in superconductors and may be selectively suppressed by application of a strong magnetic field in order to identify their contribution to the unique characteristics of superconductors. In some regions of the complex phase diagram of superconductors, the material repels the magnetic field whereas in other regions, the magnetic field penetrates into the material in the form of vortices. Besides lattice-based structural anisotropy which is common to superconductors, lattice defects such as impurities and dislocations interact with the vortices. In particular, in so-called trapped flux magnets (TFMs) these defects immobilize the magnetic field vortices, thus pinning the magnetic flux and creating an unusually high magnetic field. A TFM is activated by a strong pulsed magnetic field. In order to reproducibly create and stabilize TFMs for a long time by dedicated defect engineering, it is essential to understand the structural foundations and field-dependent dynamics incl. elastic and thermal effects during activation and subsequent relaxation by use of *in situ* scattering and diffraction techniques on the relevant ultrafast time scales. In general, high photon energies are crucial for investigating how high-temperature superconductors and other materials respond to strong pulsed magnetic fields because of space limitations: the field strength between two magnetic poles is inversely related to their distance, so that the opening window for the scattering signal is narrow when very strong magnetic excitation is required. As reciprocal space is compressed when recorded by high energy X-rays, the new XFEL facility will provide a sufficiently high Q range for reliable structural analysis on a time scale shorter than an individual magnetic pulse whose length inversely scale with the magnitude of the field. The high fluence of the XFEL radiation from an individual photon pulse also drastically shortens the measurement time from what today is many hours to less than a second. Actually, TFMs are ideal candidates to realize more favorable magnet geometries for these kinds of strong pulsed magnetic field studies as they have an equivalent field strength to conventional magnets in a significantly smaller size or higher fields at an equivalent size. In addition to exhibiting extraordinary magnetic properties, for more general applications, they are composed of earth-abundant elements, e.g. MgB_2 and rare-earth free yttrium barium cuprate (YBCO) and thus have an advantage over the more scarce permanent magnet materials.

During the fourth presentation of the session, Kristoffer Haldrup (Danish Technical University, DK) steered the attention towards photocatalysis and focused on the structural events triggered by wave-packet excitation [III. 7, III. 8]. Photophysical models exist to describe the energetic redistribution after excitation in isolated molecules, in particular for common catalysts comprising noble metals like platinum or palladium. However, the speaker stressed the vital need to include the molecule’s environment, e.g. a solvent, in any model to account for energy loss and other coupling effects to the surrounding of the catalytically active component. Only such an overall picture, an energy landscape, enables a holistic understanding of photocatalysis and eventually the rational and computational design of highly efficient photocatalytic systems. The relevant dynamical processes in the molecule start with the local effects of wave-packet excitation on the electrons on femtosecond time scale followed by the resulting movements in the average atomic structure on picosecond scale or longer. As for the environment, solute, solvation, and bulk solvent dynamics are equally important. Structural analyses based on both spectroscopic and scattering techniques are suitable to determine the desired information. While the former relies on elaborate theoretical models, the latter directly provides structural information. Given the limited size of small molecules and the disorder of molecules in solution, highly precise structural analysis of such systems by ultrafast scattering methods demands low-*Q* data with adequate reciprocal space resolution as well as high-*Q* data with good counting statistics for Fourier transformation into real space and for discerning the impact of individual model components when comparing forward scattering calculations to data. Currently, the limited energy range of the existing XFELs does not fulfill both these requirements. Access to a high-energy XFEL branch will generate the necessary data quality to reliably resolve fine structural features and would unambiguously discern the subtle differences between valid and invalid models of solute and solvent responses to excitation. Simultaneously, the XFEL pulse structure gives access to all relevant time scales of the energy flow in a photocatalyst upon its excitation. Ultimately, these capabilities will be the key to understanding what wave-packet dynamics, ultrafast inter-system crossings and couplings to the environment generate the energy-rich, catalytically active state. This will establish new highly efficient catalytic systems that comprise more abundant and cost-effective constituents such as Fe instead of noble metals.

Figure III.2 *How is energy re-distributed on internal and external degrees of freedom in photo-catalytic systems and which fundamental mechanisms determine this? Figure from reference III.7.*



In the final talk of the session, Eric Collet (University of Rennes, FR and University of Tokyo, JP) elaborated on the concept of bistability and photo-switching and illustrated a variety of examples of materials with different forms of switchable states [III.9, III.10]. For instance, in Prussian Blue, which is usually diamagnetic, irradiation with blue light induces ferrimagnetism. What these materials have in common is that the two stable states are characterized by a simultaneous change in the electronic state, e.g. spin, and simultaneously a change in the atomic structure, e.g. lattice symmetry. However, it is largely unknown which transition drives which. Femtosecond spectroscopic methods are capable of detecting transient electronic states like the ultrafast bond length expansions observed in Prussian Blue. Since the lattice is not able to respond on the same time scale, local distortions occur and evolve into global lattice expansion on the picosecond scale. When the resulting elastic waves propagate through a nanoparticle, the entire particle appears to “breathe”. These kinds of structural changes are readily recorded by ultrafast x-ray diffraction techniques. Thermal hysteresis as well as large volume changes have to be considered for the discussed photo-switching materials. The speaker highlighted how the choice of different sources of excitation, whether optical, IR or THz radiation, selectively induces specific transitions and probes electronic and atomic structure in different time domains separately. As an example, the paraelectric to ferroelectric phase transformation is triggered when applying THz radiation matching the lattice phonon mode. A future high-energy XFEL, which includes a variety of excitation options, will expand the toolbox for studying multiscale dynamics by spectroscopy at the absorption edges of high-*Z* materials as well as charge density determination and structural analysis in real space based on high-*Q* data of small particles in serial crystallography mode. Ultimately, it will be possible to image the propagation of local and global excitation effects within single particles as well as their ferroelectric response. A single laser pulse or even a single photon is sufficient to trigger the transition in suitable materials with functional bistability. With the detailed knowledge to be gained from the future facility, new concepts for electronic or magnetic nanodevices will be realized which combine high performance and low energy consumption, e.g. for memory applications similar to the phase change material-based design introduced in the first talk.

In the discussion that followed the presentations, the panel of speakers and the audience addressed some critical aspects connected to high-energy X-rays in general and XFELs in particular. By analogy to neutron beamlines, stacking multiple detectors at different positions and distances from the sample may be a comparatively cheap solution to increase *Q*-range coverage. However, there was common agreement that the scaling of the individual detector signals in intensity, background and resolution is associated with large error margins, as well as increasingly critical corrections due to geometric effects and (in particular) polarization. By experience from the community, the resulting data quality of the merged dataset is insufficient for accurate structural analysis based on weak signals and subtle changes.

On the question of the trade-off between higher flux at lower photon energies and larger *Q*-range coverage at higher photon energies, the speakers gave a clear vote in favor of high energy for their research fields. Access to high-*Q* data above 15 $Å^{-1}$ greatly increases the resolution in real space and the degree of detail gained in structural information far outweighs the lower intensity of the x-ray beam. Similarly, capturing a multitude of Bragg reflections simultaneously in one detector image substantially increases the information density and accuracy especially in single-crystal diffraction experiments. In this context, the panelists identified varying requirements for studying crystalline and amorphous or nanocrystalline samples: while the broad scattering signals from highly disordered materials are easily detectable in a setup providing moderate reciprocal space resolution, the instrumental demands are higher to resolve the sharp reflections from crystalline materials. As an example, a target photon energy of 50 keV was identified as a happy compromise between accessible *Q* range, resolution, and flux for the study of Peierls distortions in phase change materials. For mixed systems like a crystalline solid in a solvent, it is advisable to utilize two detectors, one near the sample and one farther away, to record two separate datasets with the respective optimized resolution for each component. Importantly, serial crystallography approaches, which are widely applied at XFELs, and other experiments relying on liquid jets for sample delivery, would benefit from high photon energy of the pulses as they deposit less energy by absorption and hence would significantly reduce interruption of the liquid jet (jet explosion).

The high penetration power of high-energy x-rays paves the way for new experiments on large sample volumes representing real-world processes beyond light elements such as aluminum. It was pointed out in this context that homogeneous heating (or other kinds of excitation) throughout the entire sample volume is critical and not necessarily straightforward in ultrafast pump-probe techniques. In order to comprehensively understand the impact of excitation on multiple length and time scales from local effects on the electronic structure to global effects of the atomic structure, the combination of spectroscopic and scattering techniques is indispensable. Only by extending the energy range of the available XFEL radiation will the photons match the absorption edges of high-*Z* materials, thus turning the XFEL into a spectroscopic probe for nearly all elements of the periodic table which are relevant in material science. Both the speakers and the audience emphasized that diverse, powerful pump sources providing e.g. optical, THz and IR radiation as well as electrical or magnetic fields are crucial to exploit the full potential of a high-energy XFEL facility and should be developed in parallel.

Speakers and Titles:

- Peter Zalden (European XFEL)
  Glass formation in phase change materials: the impact of a liquid-liquid transition
- Jerzy Antonowicz (Warsaw University of Technology, PL)
  Ultrafast probing of non-equilibrium melting and solidification of metals
- Zahir Islam (Argonne National Laboratory, US)
  Probing foundational to functional behaviours in quantum materials with very hard XFEL radiation
- Kristoffer Haldrup (Danish Technical University, DK)
  Understanding and improving functionality in molecular photo-catalysis with high-energy XFELs
- Eric Collet (Univ. Rennes, FR and Univ. Tokyo, JP)
  Multiscale approach of ultrafast photoinduced phase transitions in multi-functional materials exhibiting coupled electronic bistability and symmetry breaking

4 Enabling Techniques and Instrumentation for New Scientific Avenues

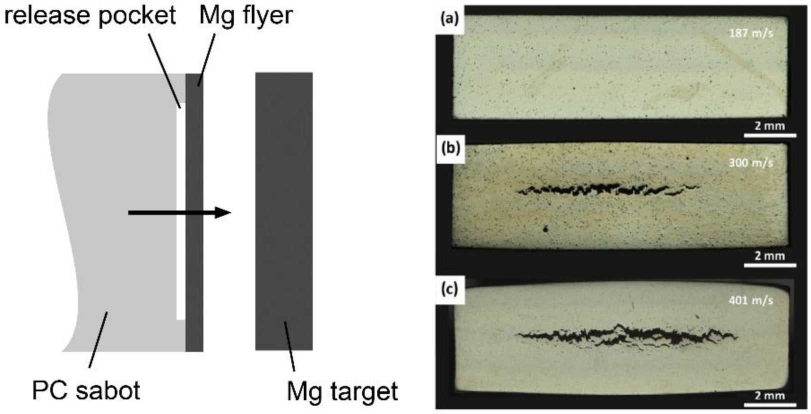
Session Chairs: David Dye (Imperial College, London), Anders Madsen (European XFEL)

In the fourth session of the Workshop, techniques and instrumentation to enable new scientific avenues were presented that would particularly benefit from access to intense, short pulse, very hard (> 30 keV) XFEL radiation (at MHz repetition rates).

The session started with a presentation by Ralf Röhlsberger (University Jena, DE) on the perspectives that would open up by increasing the maximum photon energy of European XFEL in the field of Mössbauer Spectroscopy. New nuclei would become accessible, including the particularly interesting isotopes 229-Th and 193-Ir with transition energies at 29.2 keV and 73.0 keV, respectively. Recent experiments at SACLA [IV.1] and European XFEL on 57-Fe and 45-Sc have shown the new possibilities for nuclear excitations using XFELs. For instance, the 12.4 keV nuclear resonance of 45-Sc has been detected for the first time in experiments at the MID station of European XFEL. Extending Mössbauer spectroscopy to Ir and Th could give new insight into phase transitions of iridates and extreme metrology with ultra-precise atomic clocks, respectively. For instance, the gravitational redshift could be measured due to the ultranarrow bandwidth of 229-Th with an accuracy on the order of one zepto-eV (10^{-21}). This isomeric state is at 8.3 eV above the nuclear ground state and could possibly be pumped via the 29.2 keV resonance of this isotope [IV.2] due to the ultra-high spectral brightness at high photon energies of the proposed superconducting afterburner. There is a worldwide hunt for this transition at the moment due to fascinating potential applications, e.g., for nuclear clocks or extreme metrology on concepts of cosmology like temporal variation of fundamental constants [IV.3]. The P01 beamline at PETRA III runs a successful program on nuclear scattering based on 193-Ir [IV.4] with applications in the development of OLEDs and green chemistry. There is the potential to take such experiments to the next level with a successful program at European XFEL.

In the following presentation, Alexander Rack (ESRF, FR) explained how depicting fast processes inside opaque specimens by means of ultra-high speed X-ray imaging opens a plethora of new scientific opportunities, especially in the fields of materials research and engineering. Common examples include failure in natural and man-made materials (earth quakes, fracture in engineering devices) but also fundamental research such as mechanisms of shock wave propagation or fluid dynamics such as cavitation. It is proposed to perform ultra-high-speed radioscopy enhanced by X-ray phase contrast using the high-energy option in the range 40-70 keV. Current user programs pursued at state-of-the-art synchrotron beamlines, such as 32-ID (APS, USA) and ID19 (ESRF, France), already demonstrate the enormous potential, but the capabilities can be substantially enhanced with higher photon flux and high X-ray energies above 40 keV. At European XFEL a unique end station would enable imaging studies with higher spatio-temporal resolution, eventually also coupled with diffraction techniques. Studies of formation and control of crack propagation in semiconductor materials by means of (Bragg diffraction) imaging need higher resolution to depict the nature of the crack phenomena while high photon energies are required to go beyond standard materials such as silicon [IV.5]. Further applications include experiments using an external pump, such as an optical laser, to launch a shock wave which can lead to surface modifications of engineered components, and experiments where a large sample area must be surveyed with high resolution in time and space to locate random events. The latter is needed to study spontaneous failure [IV.6]. Applications also cover studies with energetic materials used in mining, failure in alloys, and studies of auxetics i.e. materials with a negative Poisson’s ratio. The higher energy option would extend the studies to heavier metals than those studied today, for instance (laser) processing of Cu and Fe based alloys which have enormous economic importance. Parallel beam microscopy studies have been initiated at European XFEL [IV.7] and with the proposed increase in brightness in the range 40-70 keV a new era could be entered. Efforts to achieve multi-protection imaging are ongoing and together with the proposed upgrade it would provide access to phenomena that are out of range for microscopies today.

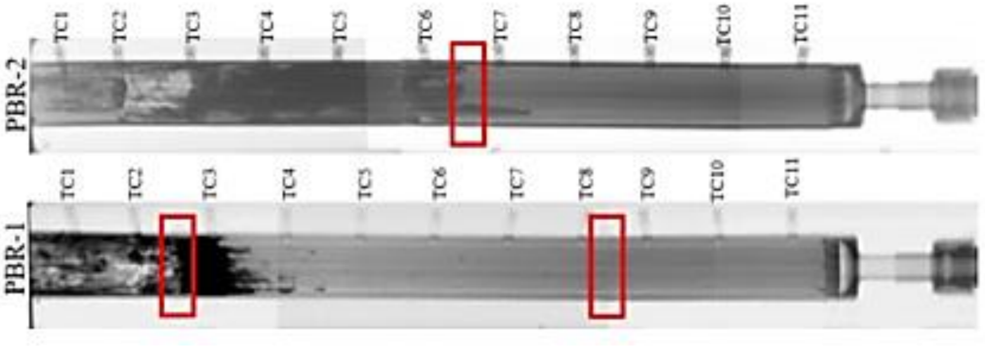
Figure IV.1 *Dynamic tensile failure in engineering alloys. The superposition of unloading waves results in dynamic tensile failure (spall). Traditionally diagnosed using combination of velocimetry and recovery techniques. Figure from reference IV.8.*



The talk by Simo Huotari (University of Helsinki, FIN) focused on the potential applications of Compton scattering, one of the dominant interaction mechanisms at high photon energies especially in light elements. Instead of considering them as unwanted background, measurement of Compton scattered photons can be used to study the momentum density of the occupied states of the valence electrons [IV.9]. Coupled uniquely at European XFEL to the ultrahigh time resolution in pump-probe experiments, Compton scattering can provide novel information on chemical bonding dynamics in molecular systems [IV.10], Fermi surfaces of metals [IV.11] and high-Tc superconductors [IV.12], spin magnetic moments of individual orbitals [IV.9], as well as electronic structure of energy materials [IV.13] and even operational devices such as batteries [IV.14]. In Fermi surface studies, Compton inelastic scattering provides complementary information to information from ARPES, with the advantage that Compton scattering is bulk sensitive, able to determine the 3D Fermi surfaces, and applicable in extreme conditions and high magnetic fields. The spin magnetic moment of individual orbitals can be measured using the sum rules of magnetic Compton scattering with circularly polarized light [IV.9]. Compton scattering studies can be carried out on gases and liquids, and on ordered and disordered solids such as high-entropy alloys [IV.15] or liquid metals [IV.16]. Water research would especially benefit from the unique access to the electron momentum densities that reveal novel properties of the electronic wave functions and states [IV.17, IV.18]. Compton scattering can also be combined with imaging [IV.14, IV.19]. Compton spectroscopy experiments can to some extent utilize the already existing spectrometers and detector development at XFEL. An optimized setup could easily be installed as a side station at any high-energy end station.

In her talk, Leora Dresselhaus-Marais (Stanford University, USA) addressed the potential of harder XFEL radiation to increase the relevance of diffraction microscopy and other types of microscopy in the characterization of materials and of phenomena that are currently inaccessible. She took as her example the challenges encountered in the steel industry, which are of utmost importance for manufacturing (automotive, construction, etc.) and engineering. Steel production is forecast to increase significantly, to enable the green transformation that is going to accelerate in the next decades. Thus, suitable approaches to transition steelmaking to emissions-free approaches is essential to reach net-zero by 2050. The 40-70 keV range could be used in dark-field x-ray microscopy to obtain 3D images of the structure and process performance with high time-resolution. It could allow penetration of reactor walls required for *in-situ* studies of many industry-relevant processes with operando transmission X-ray microscopy, X-ray diffraction, or spectroscopic methods. This could for instance help in improving the energy efficiency and lowering the CO_2 emission of the current steel production by moving from blast furnaces to direct iron reduction by hydrogen. *In-situ* X-ray microscopy tools at harder X-ray energies are very much needed to assist this transition towards a more sustainable production to study the effect of varying process parameters on the material properties. The spatial and temporal resolution that can be combined at the proposed novel source at European XFEL would provide unprecedented possibilities for multi-scale investigations, from atomic dislocations to macroscopic 3-dimensional dislocation structures.

Figure IV.2 *High photon energy and high penetration depth at XFELs could offer measurements in real reactors in operation, and provide insight into how physical phenomena scale in industrial systems. Figure from reference IV.20.*



In the last presentation of the session, Ichiro Inoue (SACLA, JP) described how materials science crystallography on small unit-cell compounds will benefit from the higher photon energy. This will provide a larger fraction of reciprocal space per exposure and hence more Bragg peaks will be captured for indexing. This is essential for serial femtosecond crystallography and in ultrafast pump-probe investigations that are only possible using free-electron lasers [IV.21]. It was also pointed out that the contraction of reciprocal space and penetration power provided by harder X-rays are essential for experiments where the sample environment provides strict geometrical restrictions, e.g. for high-magnetic field studies of novel phase transitions or high-pressure studies in diamond-anvil cells. High power laser studies or pulsed magnetic field experiments [IV.22] with very low rep rate (~1 experiment per 30 min) will also benefit in success rate due to the larger fraction of reciprocal space that can be captured per shot. Particularly, if the detector needs a certain “safety distance” to be protected against debris or stray fields the availability of harder X-rays can become decisive. Finally, it is pointed out that QED-related high-field experiments will benefit from the harder X-ray energies. For instance, photon-photon scattering processes might become detectable with the proposed upgrade of European XFEL providing a contribution to a field of science which is new for XFELs.

Speakers and Titles:

- Ralf Röhlsberger (University Jena, Germany)
  Scientific Opportunities with High-Energy Mössbauer Transitions
- Alexander Rack (ESRF, Grenoble, France)
  MHz radioscopy using hard synchrotron radiation: instrumentation and applications
- Simo Huotari (University of Helsinki, Finland)
  Inelastic X-ray scattering at high photon energies. Compton scattering
- Leora Dresselhaus-Marais (Stanford University, USA)
  Opportunities for Sustainable Metallurgy with High-Energy XFEL Microscopy
- Ichiro Inoue (SACLA, Japan)
  Enhancing capabilities of XFEL scattering techniques by short-wavelength radiation

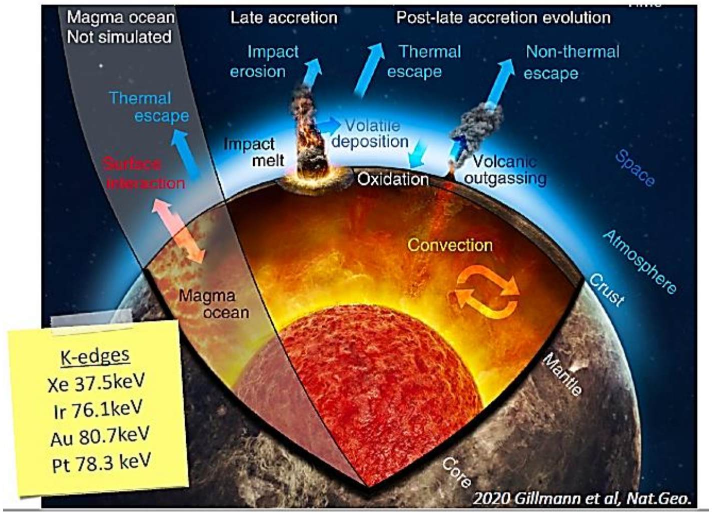
5 High Pressure, Planetary Science and Geology, Electron Dynamics, Warm Dense Matter, Relativistic Laser Plasma, Strong Field Science

Session Chairs: Alessandra Benuzzi (LULI, FR), Sergey Pikuz (HB11, Australia), and Ulf Zastrau (European XFEL)

The combination of X-ray free electron lasers with intense energetic pulsed lasers has started to revolutionize the experimental investigation of matter at high energy densities that are comparable to the interiors of planets and stars and numerous applications transiently requiring such conditions [V.1]. With future sources possibly going beyond the current world record set by the European XFEL at 25 keV, new methods for characterizing matter of extreme energy density will become available.

The first three speakers in this session, Justin Wark (University of Oxford, UK), Dominik Kraus (University of Rostock, DE) and Tommaso Vinci (LULI, FR), all addressed the potential of higher photon energy XFEL radiation to provide unprecedented insights into structure and chemistry at extreme P/T conditions: planetary interiors, planet formation, geoscience and new materials. The benefits for research in these scientific areas, addressed by dynamic compression coupled to various X-ray diagnostics (X-ray diffraction, X-ray absorption and X-ray Raman spectroscopy), were highlighted. Coupled to higher photon energies, XRD in particular has great potential to probe laser compressed liquids relevant for planetology. Examples were illustrated relevant to investigation of interiors of Neptune-like planets and the Earth. In the latter case, properties of liquid silicates under high-pressure and high-temperature conditions are critical for modeling the dynamics and solidification mechanisms of the magma ocean in the early Earth, as well as for constraining entrainment of melts in the mantle and in the present-day core–mantle boundary [V.2].

Figure V.1 *XAS investigation of the local order and valence state in high pressure silicates doped with Ir or Au could shed light into the origin of the depletion of volatile elements compared to primitive meteorites. Figure from reference V.3.*



In this context, very hard X-ray diffraction will be more compatible with containers for liquids that limit the angles. The Q-range of X-ray diffraction patterns will increase, leading to higher spatial resolution in the determination of atomic structure. The identification of liquid structure will allow a better understanding of the generation of planetary magnetic fields. Dynamic compression coupled to X-ray absorption is also opening new interesting perspectives in geophysics. To a first approximation the chemical composition of the bulk Earth bears great similarities to primitive meteorites. However, Earth shows a much stronger depletion of the moderate to highly volatile elements compared to chondrites [V.3]. There are many open questions that need to be addressed. Is this due to early planet formation or later accretion? Have gases escaped the atmosphere in the early stages of planet formation, or are they still stocked in deep layers? In this puzzling situation, XAS could give an important input since it is element selective and would track local order and the valence state under high pressure silicates doped with Ir or Au (K-edge energies at 76.1 and 80.7 keV).

X-ray Raman spectroscopy is being used to address the chemistry of low Z elements in rocky planets and during impacts [V.4]. Here hard X-rays will penetrate thick, high-density matter and extend this promising technique to heavier elements such as iron, while simultaneously measure precise X-ray diffraction. This is also interesting for investigating novel materials such as metal hydride high Tc superconductors and nanodiamond synthesis. In addition, hard X-rays could be used to discover new phases in solid matter at extremes densities and pressures (above 400 GPa) in pioneering experiments. A good candidate could be BC8 carbon which is theoretically predicted at pressures > 10 TPa.

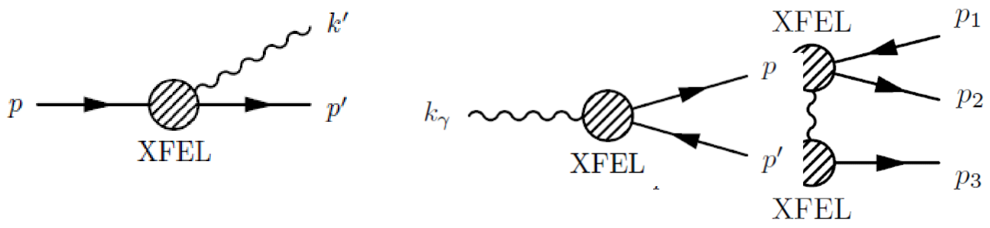
In addition to the above, the first three speakers also addressed the unique capabilities for probing large volumes and very dense matter. These are all relevant for research in inertial confinement fusion (ICF), diagnostics of implosion symmetry, convergent geometries, and materials science.

Access to sufficiently intense hard X-ray pulses will extend imaging methods to the investigation of heavier materials, very highly compressed matter and larger volumes. This will allow measurement with unprecedented precision of hydrodynamical instabilities involved in many different physical situations and in particular in ICF implosion. In this context, it is interesting to note that at ~50 keV the cross section for radiation-matter interaction for light elements (C, N, O) starts to be dominated by Compton scattering. In this case, X-ray radiography becomes a very efficient diagnostic for electron density. For this, an energetic laser (>kJ) will be necessary to achieve densities both relevant for these domains and to achieve a good contrast. A way to explore higher densities using convergent geometries is proposed and worth investigating. Measuring density-temperature-ionization conditions by spectrally resolved X-ray scattering is another very appealing diagnostic for characterizing matter. For elements of interest within stellar atmospheres [V.5] such as carbon, the main inelastic features will be well separated from elastic scattering using hard X-rays, simplifying the interpretation. Finally, a few examples were given showing opportunities in materials science, where harder X-rays open the possibility to perform transversal radiography, probing much more important volumes. Observation of late time scales of spallation will require hard X-rays at MHz rates.

In the fourth talk, Florian Condamine (ELI Prague) presented perspectives opened by higher energy XFEL radiation in the fields of atomic physics, collisional-radiative properties of high-Z plasmas, non-LTE, ionization dynamics and radiation transport in stellar interiors. Ionization Potential Depression (IPD) studies represent a relevant example of interest for XFELs in atomic physics [V.6]. For IPD, the concept of bound or free electrons in solids and dense plasmas needs to be refined to different degrees of localization. The X-ray measurements determine the fs collision dynamics between ionization states during the Auger decay time. While current studies focus on low-Z elements, going up the periodic table will require harder X-rays, which is ultimately important for the ICF community. There are also high-Z impurities in (exo-) planets which require hard X-rays to access their K-edges. The collisional-radiative properties of high-Z elements is a fundamental scientific challenge. The Z-range around gold is of particular interest due to the presence of these elements in many fields related to high-energy density physics (HEDP) but also, for example, in magnetic fusion confinement research. In addition, the ionization state distribution in high-Z plasmas is very diverse and less predictable, as it does not stagnate at the He-like states like in low-Z plasmas. Indeed, these high-Z plasmas are very transient due to the very high electron temperature that would be needed to reach K-shell charge states. Therefore, we need experimental data to benchmark models of non-LTE plasmas containing high-Z components. At the relevant temperatures, the high-Z transitions are only excited by the hard X-ray FELs, but not thermally, which makes it a clean probe. The radiation transport in stellar interiors can be addressed with X-ray heating at high densities. Moreover, the energy selectivity of XFELs isolates specific transitions within a complex multi-component plasma with a complex ionization distribution. For studying very complex population and frequency redistribution processes at high Z, a self-seeding scan of specific spectral lines is ultimately required.

The last speaker of the session, Uwe Hernandez Acosta (HZDR, DE), covered perspectives in Strong-Field Science. He presented examples of the application of a 50 keV XFEL for strong -field physics, modelled by the interaction with an electron beam. The process of electron-positron pair production in strong fields deviates from the well-known perturbative result in weak field backgrounds. In a strong field background, an electron can directly emit a photon which in turn can generate an electron-positron pair via the trident process. Using 50 keV photons, only about 5 MeV kinetic electron energy is required to reach the trident threshold, which is available by electron guns or laser acceleration (in solids, or wakefield) [V.7]. The trident process can also be used to test models for dark matter candidates [V.8]. Using the proposed massive “dark photon”, the assumed mass and coupling to ordinary matter could be determined more precisely than with hadron experiments. Certain exclusion regions can be scanned, but the trident experiment could also be used to detect dark matter (instead of excluding certain mass/coupling ranges) because there is full control over the QED background. A second scheme is the interaction of hard X-rays with electrons in the presence of an intense, infrared few-cycle laser light field. It allows us to study laser-assisted Compton scattering, Breit Wheeler pairs production and trident, where during the peaks of the few-cycle IR laser field, spectral features are introduced. A (quasi-) continuous X-ray beam (as in a synchrotron) is not sufficient for strong-field studies as high intensity is required. A user community, similar to established synchrotron or XFEL users, may not exist yet. Many colleagues work on theoretical models, but more experimentalists will emerge with upcoming experimental capabilities at XFELs. The LUXE experiment at DESY, and the detection of QED vacuum birefringence at HED/HIBEF, European XFEL, are examples of such developments.

Figure V.2 *Using the XFEL as a driver: Compton scattering (left), Breit-Wheeler pair production (center) and the trident pair production (right).*



Throughout the session, a few technical aspects were discussed. In particular, there was a general agreement that split-delay capabilities would be very important given that most processes occur on the fs to ps timescale.

On the other hand, MHz capability is required for specific areas where T-induced or P-induced phase transitions are investigated using the diamond anvil cell (DAC) platform, or for observation of processes in the ns to ms timescale (spallation, ejecta, and fracture formation) by MHz microscopy. Spatial coherence is identified to be important for X-ray photon correlation spectroscopy experiments to measure transport coefficients in warm dense matter. Finally, it was underlined that the opportunities opened by higher energy XFEL radiation would be particularly important if coupled to a very energetic laser (>kJ) and/or with a convergent geometry.

Speakers and Titles:

- Justin Wark (University of Oxford, UK)
  Implications of High Photon Energy FELs for some areas of HED science
- Dominik Kraus (University of Rostock, DE)
  X-ray spectroscopy, diffraction and imaging techniques for high energy density matter enabled by very hard X-rays at XFELs
- Tommaso Vinci (LULI, FR)
  Hard XFEL radiation for warm dense matter, high energy density studies
- Florian Condamine (ELI Prague, CZE)
  Study of heavy elements collisional-radiative behavior using hard XFEL radiation
- Uwe Hernandez Acosta (HZDR, CASUS, DE)
  Strong field physics prospects at 50 keV at European XFEL

6 Conclusions

The workshop was a very lively forum for discussion and exchange on the new scientific opportunities that will open up with the availability of harder XFEL radiation. We saw throughout the five sessions how this capability will address science questions that are out of experimental reach today in many different areas of application, from catalysis to the steel industry, from planetary to strong field science. But most importantly, harder XFEL radiation will enable further new developments for understanding how materials behave under a large range of conditions. This understanding is key for providing a 'reality check' on theoretical models of materials, where new insights will require the next level of detail and resolution in time, energy, and space. Such models are our best attempt at understanding and predicting how materials perform and how we may influence their properties. Improving models is the key step in the rational path towards the development of new materials with enhanced energy efficiency and performance.

6.1 Science Opportunities of high energy, ultrashort XFEL pulses

High Q-range coverage: Enables (fs time resolved) high resolution tracking of structural dynamics in disordered materials (e.g. for chemical reactions in solution and glassy metals), through analysis of x-ray scattering, including pair distribution function analysis with high resolution and serial crystallography of small unit cell materials.

High penetration: Time resolved residual stress fields, delamination and fissure propagation in materials, such as carbon fiber-reinforced polymers and metals. Study of irreversible processes within realistic environments in hierarchically organized materials: plastic deformation or martensitic phase transformation in metals, switching of domains in ferroelectrics, flux lattices in superconductors, biomineralization in bones, flow in geomaterials, 3D printing

Access to K-edge spectroscopy of high-Z materials: Enabling tracking of chemical dynamics for high-Z materials and for high-Z materials under extreme (hot dense) conditions.

Reduced radiation damage: Allows imaging stochastic phenomena in heterogeneous samples. It might also provide a way to reduce the problem with unstable, exploding jets for liquid flow samples, which limits the usable repetition rates for x-ray scattering experiments.

Although the discussion at the workshop focused on science, it was emphasized that research and development for undulators, detectors, optics, diagnostics and pump sources to match the new XFEL capabilities was critically important, and is indeed an integral part of the European XFEL 2030+ Strategy.

6.2 Potential and Emerging Technologies

The workshop showed how very hard energy XFEL radiation can contribute to the development of new diagnostic tools and techniques for monitoring and optimizing materials which may provide new solutions for information storage and lead to lower life cycle impact thus enabling a cyclic economy both for materials for construction and for materials with specific functionalities.

It was discussed how such tools and techniques can contribute to clean energy by enabling advanced materials science in areas relevant for energy storage, such as batteries and supercapacitors, as well as materials for solar cells, fuel cells, and other renewable energy technologies. For example, studying catalysts at the atomic scale can lead to the development of more efficient and effective catalysts for processes like carbon capture and storage, hydrogen production, and other energy-related applications. Using the new capabilities will also enable the study of a new range of materials under extreme conditions, such as high velocity impact, pressure and temperature, important for the development of fusion power, planetary security and spacecraft protection against debris.

6.3 Potential New Communities

Each session addressed the potential for expanding existing user communities, and even reaching out to new scientific communities that are not orbiting around XFELs today. Three areas were highlighted as being the most likely to succeed in this endeavor: chemistry - attracted especially by *ultra fast*-PDF, materials science (including under extreme conditions) – attracted by the unmatched high penetration power and high Q_{max} - and Extreme Fields science, today well supported by theory but lacking a community of experimentalists that is expected to emerge with the upcoming experimental capabilities at XFELs .

6.4 Outlook

With its already existing lead in high energy XFEL capabilities, the European XFEL is uniquely qualified to drive this emerging field with major scientific, technological and societal impact on an international scale. To realize this potential, clear decisions are needed towards developing and implementing new, superconducting undulator technologies and towards supporting development of new accelerator and detector capabilities. This must be followed up by a solid strategy for their realization and exploitation.

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A Report from 28th Scientific Advisory Committee (23-24 March 2023)

The 28th SAC met for a hybrid format meeting at the European XFEL on 23-24 March 2023. Scientific Director Sakura Pascarelli presented the outcome of the Workshop in a short (20 minute) presentation, which was followed by a lively discussion. The relevant extract of the 28th SAC report is copied below.

"SAC appreciates the substantial insights gained at the hard X-ray science workshop, and is pleased to recognize the breadth and impact that high brilliance hard X-ray XFEL pulses could have for the different science cases covered, including applied materials and industrial applications, structural dynamics in disordered materials, dynamics of functional materials, high pressure, planetary science and geology, electron dynamics, warm dense matter, relativistic laser plasma, and even strong field science (trident process, dark matter).

Lasing in the high energy X-ray range beyond the currently achieved 30 keV and the systematic development of beam delivery, optics, instrumentation (including in particular detectors) and method development all pose significant challenges which require concerted and sustainable efforts. European XFEL is in an excellent position to meet these challenges and to develop this potential. This would capitalize on European XFEL's unique selling point as the world's highest-energy high-current SCRF electron accelerator, on the machine group (DESY) competence and potential to deliver high pulse intensity at high photon energies, and on exploiting a hard -ray burst-mode.

> ***Recommendation 28-08****: SAC recommends XFEL to develop a comprehensive, phased, development strategy that would open up new capabilities for several important fields, which could become a strategic priority for XFEL. This should include a more detailed assessment of the science opportunities (and priorities) and the associated*

> *experimental requirements. Contrarily, not starting such a process in this direction would likely be a significant missed opportunity.*

The presentation covered a wide range of science opportunities. Many are in the field of materials science, looking at real large-scale materials that benefit from the deep penetration of the high energy X-rays. A good number of the science areas represent pump-probe measurements, which poses a question about the ability to pump large-scale materials' volumes, which is limited by laser/electron penetration. An interesting potential approach could the development 2-colour capabilities where the samples can be pumped with softer X-rays that can be filtered out before the high energy X-ray detector.

For the Pair Distribution Function (PDF) method, there is a specific threshold in momentum transfer needed to resolve the bond lengths associated with disorder processes that can be excited on a ps time scale. That threshold is around 20 $Å^{-1}$, which can be reached at 40 keV. For time-resolved PDF, it will be useful to consider representative "flagship" science experiments to better define all the experimental requirements (e.g. matching required resolution, photon energy, and achievable instrument time response) for addressing the highest-impact science. This should include considerations on sample thickness and pumping schemes that are most relevant to the science."