Towards pump-probe resonant X-ray diffraction at femtosecond undulator sources

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Abstract. The first tunable undulator source for femtosecond hard X-rays in the range 4–12 keV is now in operation at the SLS storage ring. The source combines accelerator and laser technology relevant for future seeded free electron lasers. It provides inherently synchronized femtosecond laser ‘pump’ and X-ray ‘probe’ pulses to enable time-resolved diffraction and absorption experiments. By using X-ray diffraction to probe laser-induced coherent optical phonons in bulk bismuth, we estimate an X-ray pulse duration of 140 ± 30 fs FWHM with timing drifts below 30 fs rms measured over 5 days. The excellent spatial and temporal stability of the source allows quantitative measurement of ultrafast lattice dynamics and associated phase transitions in real space with atomic resolution and instrumental time resolution of 85 fs rms. Studying semimetals such as bismuth, we have demonstrated (i) grazing incidence femtosecond X-ray diffraction on single crystals that allows us to more completely characterize the ultrafast structural dynamics of solids, and (ii) optical control of real space coherent atomic motion. Both methods will be used to study the dynamics of photo-induced phase transitions in strongly correlated systems such as manganites. The time resolution of such measurements could be improved by one order of magnitude at future XFEL facilities at much higher flux. Femtosecond linear and non-linear resonant X-ray scattering employing full polarization control both in the soft (0.3–3 keV) and hard (4–15 keV) X-ray regime will become feasible which allows direct measurement of orbital degrees of freedom. However, a laser and hard X-ray cross-correlation technique with sufficient temporal resolution and signal-to-noise ratio appropriate for single shot operation has yet to be realized. Again, laser seeding using a phase stabilized few-cycle (5–7 fs) laser may be a viable option to generate <10 fs X-ray pulses.

1. Introduction

The aim of femtosecond (fs) X-ray pump-probe (XPP) diffraction or absorption experiments is to capture transient structures when matter rearranges on the atomic scale. In an XPP experiment structural changes are typically stimulated by a femtosecond pulse of optical or far-IR laser light, and these changes are observed using X-ray scattering techniques. To achieve sub-picosecond time resolution, both an ultrafast X-ray source (or an ultrafast X-ray detector such as an X-ray streak camera) and femtosecond-level synchronization between the optical laser and the X-ray pulse must first be developed. As demonstrated by a recent UV-pump and NIR-probe experiment to track the electron dynamics in atoms and molecules with sub-fs (attosecond) time resolution [1, 2], there is considerable experience with laser-based sources of pulsed light concerning control of the pulse length, the relative time delay and the relative spatial position between the pump and probe beams.

Today most results on the ultrafast structural dynamics of condensed matter by diffraction have been obtained with laboratory based sources. Initial work on X-ray plasma sources used high-intensity lasers with low pulse repetition rates of 1–20 Hz [3–8]. Recently developed plasma sources with kilohertz repetition rate provide Cu-K α emission (8 keV) of nearly 10^6 photons/s on the sample with spot size $\approx 30 \mu\text{m}^2$ and X-ray pulse duration 500 fs FWHM [9–11]. This development has opened the way to measure subtle, fully reversible structural changes of coherent atomic motion in nanostructures [12], coupled ultrafast lattice and polarization dynamics in ferroelectric nanolayers [13], and the ultrafast rearrangement in a molecular crystal in response to a local dipole change [14]. Ultrafast electron diffraction, another area of development of compact sources, is evolving hand-in-hand with X-ray techniques. A laser photocathode can be incorporated in a microscopy apparatus [15] to generate 320 ± 120 fs FWHM electron pulses below the space charge limit (500 electrons/pulse). Despite the large group-velocity mismatch between the non-relativistic electron pulses (30 keV) and the laser, sub-picosecond (sub-ps) time resolution is achieved by tilting the laser wave front. This technique has been used to study nonequilibrium structural phase transitions in superconducting cuprates [16]. In a second

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experiment [17], a direct connection between the dilation of the V–V bond in single crystal vanadium dioxide (VO₂) and the equally fast changes in conductivity measured with broadband THz spectroscopy [18] has been established.

The situation is different at undulator based sources where relativistic electron beams are used to generate highly collimated X-ray beams. This approach has the potential to provide tunable X-ray sources for both the soft (0.3–3 keV) and hard (4–15 keV) X-ray regime exhibiting a pulse duration in the range 10–100 fs or below, full (spatial and temporal) coherence, flexible (linear and circular) polarization, and a high photon flux of 10^{12} photons/pulse. But there are new challenges. The macroscopic length scales (>30 m) needed to generate micron size X-ray beams make the spatial and temporal stability required at the experimental station non-trivial tasks. Because only a few accelerator based sub-ps X-ray sources exist today, the number of fs XPP experiments at such sources is scarce. Demonstrated performance at low intensity sources therefore is needed for the design of future XPP experiments at X-ray free electron laser (XFEL) facilities which are now under construction [19–21]. Despite the low radiation extraction efficiency $\varrho \simeq (5 - 10) \times 10^{-4}$ at 1 Å, an XFEL can provide 10–20 GW coherent (saturated) power $P_{\text{sat}} = \varrho I_p E_b / e$ due the high power stored in the electron beam ($E_b = 6 - 15$ GeV is the beam energy, $I_p = 2 - 5$ kA the peak current and e the electron charge). To provide such power levels there is no alternative to undulator sources in the foreseeable future.

We report on our ongoing work, namely to develop X-ray undulator sources, diagnostics and experimental techniques to pursue femtosecond resonant XPP diffraction on strongly correlated systems. Progress in this field is intimately connected with the technical development of tunable X-ray sources exhibiting good spatiotemporal stability, sensitive diagnostics on timing and synchronization to correlate the laser-electron and laser-X-ray interaction on the femtosecond time scale, and experimental techniques to capture the structural and electronic dynamics on such a time scale with atomic spatial resolution. Section 2 summarizes the motivation of our work. As described in section 3, we rely on laser manipulation of relativistic electron beams to generate sub-ps X-ray pulses. This approach combines undulator and laser technology, two areas where major progress has been made in the recent past. In section 4 we report on the performance of our present low intensity source which has recently been commissioned and is now routinely operated at the SLS storage ring with a 2.4 GeV electron beam [22]. We believe that for an XFEL at PSI (PSI-XFEL), which currently is in its design phase, this approach can be extended to linear accelerators (linacs) as drivers of amplified, coherent radiation in a long undulator using a 6 GeV electron beam [23]. For measuring the pulse duration of sub-ps electron bunches we exploit the temporal coherence of the radiation emitted in the far infrared (IR) spectral range (section 5). XFEL radiation is then discussed as coherent radiation emitted by electrons bunched at the Angstrom length scale. In section 6 we outline first femtosecond

XPP experiments on Peierls distorted solids and manganites. In section 7 we discuss those topics which are of relevance for our work once seeded XFEL radiation will be become available. A summary and conclusions are given in section 8.

2. Motivation

A significant challenge in condensed matter is understanding the dynamic interplay between atomic and electronic structure. In such systems, the strong interplay between valence charge distribution, orbital order, spin orbit, and subtle distortions of the atomic lattice give rise to complex phase diagrams. Material properties such as superconductivity, metal-insulator transitions, colossal magnetoresistance and multiferroicity are observed. Time-resolved X-ray measurements on the fundamental time scale underlying such correlations should offer new physical insights by separating correlated effects in the time domain while providing direct information about the atomic and electronic structure. The vibrational period $\tau_{\text{vib}} \sim 10 - 100$ fs is the fundamental time scale for atomic motion in crystallographic phase transitions such as solid-solid transitions, changes in or between unit cells, and symmetry breaking (dimerization and cell doubling). The electron-phonon interaction time $\tau_{\text{e-ph}} \sim 1$ ps, the electron-electron scattering time $\tau_{\text{e-e}} \sim 10$ fs, and the electron correlation time $\tau_{\text{e-corr}} \sim 0.1$ fs are the relevant time scales for electronic structural dynamics in metal-insulator, ferroelectric-paraelectric, ferromagnetic-paramagnetic phase transitions, and charge-orbital ordering phenomena. Femtosecond X-ray scattering methods will allow separation of correlated phenomena in the time domain and the observation of the underlying correlations in real space as they develop. Bragg diffraction provides information about long-range order in crystalline systems. Since X-rays interact with core level electrons, they provide direct information about atomic position and bond lengths. Time-resolved XPP diffraction is therefore a promising tool to study optically stimulated structural changes in complex systems on the fundamental time scale of fluctuations in the vicinity of the transition point during a phase transition or ordering process. However, regular XPP lacks sensitivity to electronic structural dynamics. To overcome this problem, we propose to develop time-resolved pump-probe resonant X-ray diffraction (RXD) by combining XPP and RXD techniques. In the last 10 years RXD has developed into a powerful technique to obtain direct information about charge, magnetic, and orbital degrees of freedom. It combines the resolution of X-ray diffraction needed to determine long-range ordered structures with element specific sensitivity of X-ray absorption to probe local electronic configurations by tuning the X-ray energy to characteristic absorption edges.

The electronic and magnetic properties of complex materials as three dimensional $R_{1-x}A_x\text{MnO}_3$ and layered $R_{1-x}A_{1+x}\text{MnO}_4$ manganites (R: trivalent rare earth, A: divalent alkaline earth) are thought to be due to competition among mechanisms that influence the localization of electrons occupying partially filled 3d orbitals. Trapping

due to structural distortions (*e.g.* Peierls- and Jahn-Teller distortions) and mutual repulsion (Coulomb and spin correlation effects) tend to localize 3d electrons on the transition metal site. At the same time there is a tendency to minimize electron kinetic energy by delocalizing the electrons over many atomic sites by hybridization with oxygen $2p$ orbitals. This subtle balance can be influenced by chemical doping. For example, the use of chemical doping to increase the density of conducting electrons can cause an insulator-to-metal phase transition due to the relaxation of structural distortions. Because photoexcitation rearranges the occupation of different orbitals in a manner analogous to chemical doping, excitation with light can transform the structural, electronic and magnetic properties of a complex solid. In a recent optical experiment, the correlated charge and spin dynamics in perovskite manganite $\text{Gd}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ have been measured during a femtosecond photoinduced phase transition from an insulator with short-range charge and orbital order (OO) to a ferromagnetic metal [24]. To establish in addition a clear connection between lattice dynamics and electronic properties in manganite systems, we plan to measure coherent optical phonons where their coupling to photoexcited charge carriers can be enhanced by the structural distortion corresponding to the charge-order (CO) phase transition ($T_{\text{CO}} \simeq 100\text{--}250\text{ K}$). In this way we hope to clarify if dynamic phase separation takes place in photoexcited metal-insulator, paramagnetic-ferromagnetic, and charge order phase transitions, and if so, on which time scale this happens. With our present source such experiments can be performed in the range 4–12 keV with time resolution 100–200 fs FWHM. Its high spatiotemporal stability allows to apply two methods we have developed so far, namely (i) optical control of real space coherent atomic motion, and (ii) grazing-incidence X-ray diffraction on single crystals, which allows us to more completely characterize the ultrafast lattice dynamics in comparison to fs optical reflectivity measurements or to fs X-ray diffraction on thin films by obtaining nanoscale depth-resolved data [25].

3. Short X-ray pulses: laser slicing

There are several ways to generate sub-ps X-rays at undulator sources, namely to ‘slice’ or to compress the electron

or the X-ray pulses. Each approach relies on a dispersive element to exploit an energy-momentum correlation within the bandwidth of the pulse to either spatially separate a short fraction from the core pulse in the case of slicing, or to use time-of-flight dispersion to compress the whole pulse. So far only electron bunch slicing at storage rings and electron bunch compression at linear accelerators (linacs) [26, 27] have been demonstrated. Because of its higher peak current and therefore higher X-ray flux, electron pulse compression would be the preferred method. However, in contrast to linacs which can be operated at several kilo-Amperes, the peak current (hence the bunch charge) at storage rings is limited to $\sim 100\text{ A}$ before seriously sacrificing other performance parameters of the electron and X-ray beam due to interbunch instabilities.

The layout of our experiment is shown in Fig. 1. There are several advantages over other methods of generating short pulse X-rays: (a) Ultrafast lasers can provide highly synchronized (and phase stabilized if needed) optical pulses with flexible pulse shape and polarization to generate inherently synchronized pump- and probe-beams when the X-ray beam is derived from the same sequence of laser pulses. (b) Undulators installed at storage rings provide high average flux (photon/s) and average brightness (photons/s/mm²/mrad²) which is partially coherent and tunable throughout the X-ray spectral region. The X-ray pulse length is typically 50–100 ps FWHM. X-ray characteristics such as bandwidth, tunability, harmonic content, type (linear or circular) and degree of polarization can be precisely tailored by forcing the electron trajectory to follow the path determined by the strength and geometry of the undulator magnetic field, largely independent of the pulse characteristics of the seeding laser. (c) When operated in current top-up mode and controlled by fast orbit feedback (FOFB) systems correcting the electron bunches in both transverse and longitudinal direction, storage rings like the SLS can provide X-ray beams with sub- μm position and sub- μrad pointing stability, respectively (see section 4).

Laser slicing (or seeding) relies on the fact that in the presence of a static magnetic field, an electron freely propagating in space can interact with an electromagnetic wave to either emit or absorb energy. The laser-electron interaction is fundamental to any free electron laser (FEL) and is described by the theory of a small signal gain FEL

Fig. 1. Layout of the laser-X-ray pump-probe experiment at the μXAS beamline. Travel distances are 25 (100) m for the pump (probe) branch. The FEMTO facility installed at the μXAS beamline consists of two main installations, the FEMTO insertion (or ‘slicing spectrometer’), and the FEMTO laser system. (I) Slicing spectrometer: installed in a long straight section (11 m) at the SLS storage ring, it consists of: laser injection, modulator (wiggler) for energy modulation, dispersive section (3-dipole chicane) for pulse separation, refocusing triplet, laser extraction, FOFB-corrector, radiator (in-vacuum undulator) for X-ray generation, and FOFB-corrector. ID-FF (Insertion Device Feedforward) and FOFB (Fast Orbit Feedback) corrections are applied based on BPM (XBPM) beam position readings for the electron (X-ray) beam. (II) Laser system: (1) Oscillator (30 fs, 100 MHz, 500 mW, 795 nm) synchronized to the RF master oscillator (500 MHz). (2) Pump amplifier-I (100 fs, 2 mJ, 1 kHz, 800 nm) and ‘slicing’ probe amplifier-II consisting of a regenerative amplifier and a symmetrically pumped cryo-cooled 2-pass amplifier (50 fs, 5 mJ, 1 kHz, 800 nm). Proposed future upgrade: 10–20 times higher repetition rate.

amplifier [28]. Laser seeding (using a fs Ti:sapphire laser) has originally been proposed to induce an energy modulation of the electron bunch to generate fully coherent amplified UV-light in a linac based, single-pass, high-gain high harmonic generation (HHG) free electron laser [29–31]. Later it has been realized that the same process can be used in a storage ring to impose an energy modulation on the electron beam of several sigma beyond the natural energy spread width [32]. The ‘laser slicing’ technique first demonstrated at the ALS [33, 34] has recently been implemented at BESSY [35, 36] to generate sub-ps soft X-rays (1–2 keV) with variable polarization.

In our case the static field is a vertical planar, periodic magnetic field (period $\lambda_w = 138$ mm) provided by a wiggler (the “modulator”). Although the magnetic field of a tightly focused laser beam is much higher than the static one ($B_{w, \text{eff}} = 1.9$ T) [37], its coupling to the electron beam is negligible if the electron has relativistic energy ($\beta \simeq 1$) and co-propagates with the laser beam. We note that the electron trajectory is determined solely by the static magnetic field $B_{w, \text{eff}}$ of the modulator, which can be precisely controlled. When the modulator field is tuned to the laser wavelength $\lambda_L = \lambda_w(1 + K_{\text{eff}}^2/2)/2\gamma^2$ to obtain resonance by changing the wiggler gap [38], only the electrical field of the laser couples to the electron. Because the electron has a velocity component transverse to the wiggler axis and parallel to the optical electric field, it can resonantly interact with the wave and – depending on the relative phase – will gain or lose energy. Optimal energy transfer is achieved if the number of modulator periods N_w matches the number of laser optical cycles ($N_L = 18$). According to simulations a laser pulse energy of 2 mJ provides a maximum energy modulation of $\sim 1\%$ (24 MeV).

Because of slippage of the electron bunch with respect to the laser pulse in the modulator, the energy (or charge density) modulation extends ~ 85 fs FWHM at the end of the interaction region. Due to horizontal angular dispersion in the slicing spectrometer, electrons with energy gain and electrons with energy loss separate in opposite direction, leaving a ~ 85 fs FWHM hole or ‘dark pulse’ in the core beam. As a result a longitudinal charge density modulation is induced on the electron bunch which due to time-of-flight dispersion undergoes continuous evolution as the bunch propagates along the storage ring. Coherent synchrotron radiation (CSR) emitted by the sliced electron bunches and the ‘dark pulse’ is used to derive a sensitive cross-correlation signal for the laser-electron interaction [39]. When the 50 fs FWHM laser hits the single isolated (‘hybrid’) electron bunch with charge 4 nC (2×10^{10} electrons), the number of sliced electrons is only $N_e \sim 4 \times 10^6$ due to the rather low slicing efficiency of $\sim 2 \times 10^{-4}$ per bunch. Nonetheless, due to its quadratic dependence on the number N_e of energy modulated electrons (see section 5), the CSR signal can be quite strong. At the first bending magnet, 14 m downstream of the interaction region (the location of the ‘THz-diagnostic’ port), CSR at wavelengths $> 30 \mu\text{m}$ in the far IR spectral range (1–10 THz) is detected. The spectral response ($\leq 60 \text{ cm}^{-1}$) of the He-cooled (4.2 K) InSb-bolometer used as detector allows to also record the long-wavelength coherent radiation emitted during the first turns of the modu-

Fig. 2. Tuning of the laser-electron interaction by monitoring coherent far-IR radiation (terahertz (THz) range) and incoherent sliced X-ray flux. (a) For the sliced X-rays the resonant wavelength is red-shifted because only radiation from a subset of electrons (namely with 0.6–0.8% energy gain) is accepted by the first mirror in the beamline. (b) Optimization of the temporal overlap between the laser pulses and the ‘hybrid’ single electron bunch (hybrid electron bunch filling: a single, isolated electron bunch hit by the slicing laser is placed in a 180 ns gap of the multibunch train to allow electronic gating of the detectors). As expected, a linear (square) dependence on the number of sliced electrons is observed for the incoherent X-ray (coherent far-IR) radiation channel. A pulse width of 85 ps FWHM is measured for the non-sliced hybrid electron bunch (4 mA).

lated electrons around the storage ring. CSR is ideally suited as an on-line cross-correlation signal to optimize the laser-electron interaction in terms of spectral and spatial overlap (see Fig. 2). The coherent nature is directly demonstrated by the N_e^2 -dependence of its intensities which perfectly match the incoherently emitted intensities ($\sim N_e$) squared of the femtosecond X-rays when the slicing laser is scanned across the electron bunch. An on-line CSR-diagnostic is now routinely used during laser slicing operation.

4. Femtosecond hard X-ray source: performance

FEMTO, installed at the μXAS beamline at the Swiss Light Source (SLS) at the Paul Scherrer Institut, is the first tunable femtosecond undulator source for hard X-rays [40]. It is designed to generate X-rays in the range 4–18 keV (slicing operation: 4–12 keV) based on the high harmonic (3rd–9th) operation of a small gap, short period in-vacuum undulator [41]. The design and operation of the source take advantage of its modular design to

allow laser-X-ray pump-probe experiments with time resolution of either 85 ps or 0.2 ps (slicing operation). Time-resolved experiments are performed using an isolated single ('hybrid') pulse in a 180 ns gap of the SLS pulse train to allow gating of the detectors (APDs, and 2D area detectors developed by the PSI detector group, namely the MYTHEN μ -strip detector [42] and the PILATUS pixel-detector [43]).

The FEMTO source consists of two main parts, the FEMTO laser system and the FEMTO insertion (or 'slicing spectrometer'; more details can be found in Ref. [22, 40]): The laser system consists of a femtosecond Ti:sapphire oscillator synchronized to the master clock of the storage ring followed by two regenerative amplifiers. They are operated in parallel to deliver high energy femtosecond pulses for pumping samples and for modulating the electron bunches inside the storage ring. The probe pulses are amplified in two steps: first by a regenerative amplifier and then by a symmetrically pumped 2-pass amplifier. A nearly diffraction limited spatial profile ($M^2 \leq 1.4$) for efficient slicing is ensured by cryogenic cooling of the 2-pass amplifier laser crystal. The intense femtosecond laser pulses are focused in vacuum over an optical distance of 45 m to interact with the electrons at the modulator with a Rayleigh length of 0.6 m (beam waist $w_0 = 490 \mu\text{m}$). The environmental temperature is stabilized to $<1^\circ\text{C}$. The FEMTO insertion acts as a 3-stage spectrometer. To minimize bunch lengthening, the spectrometer is placed in a single 11 m long straight section of the storage ring. The associated breaking of the ring periodicity imposes constraints on the electron beam parameters in order to avoid deterioration of the storage ring dynamic aperture [44]. The ~ 85 fs FWHM energy-modulated electrons from the modulator pass a chicane followed by refocusing magnets to allow small gap operation of the radiator (in-vacuum undulator operated at high harmonics) where the X-rays are generated. The chicane induces a spatial (± 2 mm) and angular (± 0.5 mrad) horizontal separation of the sliced beam at the radiator center. Movable apertures in the X-ray beamline at 12 m distance from the radiator block radiation from the core beam while allowing X-rays emitted by the satellite beam to pass. The signal-to-background ratio is critical for any slicing scheme. For sufficient suppression of the core beam background only radiation from electrons with positive energy modulation $\Delta E/E > 5 \times 10^{-3} \simeq 6 \sigma_{\Delta E/E}$ is accepted (where $\sigma_{\Delta E/E}$ is the natural energy spread, $E = 2.41$ GeV). Because the X-rays do not pass windows or any optical element in front of this aperture, any possible additional X-ray background from the core beam is due entirely to the magnetic elements. Several photon absorbers installed along the spectrometer as well as adjustable slits in the beamline are used to suppress the long pulse background emitted by the 85 ps FWHM core beam by $10^3:1$. The background is instead limited by the "halo" of incompletely damped previously modulated electrons [35] that limits the signal-to-background ratio to $\sim 50:1$ for monochromatic X-rays (see Fig. 3). The stability of relevant parameters for the laser, electron and X-ray beams recorded during extended pump-probe scans is shown in Fig. 4. FOFB and ID-FF

Fig. 3. Measured number of sliced X-rays per pulse in a 0.1% bandwidth at 6 keV. Due to adjustable slits in the X-ray beamline and fixed photon absorbers installed along the slicing spectrometer, background contributions from the core and halo electrons are efficiently suppressed.

corrections applied to the electron beam provide sub- μrad pointing stability for the X-ray beam.

The femtosecond sliced X-ray flux at 1 kHz repetition rate measured with an avalanche photodiode is 2×10^5 (6×10^4) photons/s in a 0.1% bandwidth at 5 (8) keV, for 2 mJ slicing laser energy and 4 mA current (60 A peak current) in a single (isolated) bunch. To obtain information on the pulse length and timing stability, we use X-ray diffraction to measure high-amplitude phonon dynamics of photoexcited bismuth [8, 45]. Strong optical excitation of the near-surface region of the crystal results in large amplitude coherent A_{1g} optical phonons, corresponding to motion of atoms along the body diagonal of the rhombohedral unit cell (see section 6). Since this motion alters the X-ray diffraction structure factor, we can observe the coherent phonon dynamics by measuring the diffracted intensity from the (111) Bragg reflection as a function of time. The X-ray energy was set to 7.15 keV and the angle of incidence to approximately 0.5° , limiting the probe depth to <15 nm due to photoabsorption in the crystal. A toroidal Rh-coated mirror with a grazing incidence of 3 mrad collimates the X-rays vertically and creates a weak horizontal focus on the sample. Close to the sample, a single elliptically bent mirror focuses the beam vertically to a size of $10 \mu\text{m}$ and a Mo/B₄C multilayer mirror selects an energy bandwidth of 1.2%. The sample is aligned so that the plane of incidence is vertical, resulting in a spot size on the sample of $300 \mu\text{m} \times 1.1$ mm. The pump laser is incident on the sample at a grazing angle of $\sim 14^\circ$, resulting in a geometrical increase in time resolution by 110 ± 20 fs FWHM. The probe signal is sampled with twice the pump frequency to record alternately pumped and unpumped diffraction data to compensate for slow baseline and intensity drifts in the source, pump laser, detector or electronics [46]. Depending on the use of a single- or double-multilayer monochromator and losses due to the refocusing optics and air absorption, the incident flux on the sample was $(2-8) \times 10^5$ photons/s. In Fig. 5 we show data on the (111) reflection (accumulated for 1.5 hours) yielding an effective time resolution of 195 ± 25 fs FWHM including time delay drifts. Fitting

Fig. 4. Slicing diagnostic chart recorded on-line over 12 hours. Monitored are (a) the electron beam position at the radiator (BPM readings) where the X-rays are generated, (b) the laser position stability at the interaction point inside the modulator (waist 980 μm) controlled by position feedback, (c) the THz intensity as laser-electron overlap diagnostic, (d) the X-ray beam position (XBPMs 8.6 m downstream of the radiator, sampling 0.1 Hz), and (e) the femtosecond sliced X-ray intensity.

these data to a simple model of a displacive excitation [47] we obtain an average phonon frequency of 2.60 ± 0.05 THz, which is comparable to measurements on bismuth thin films [45]. Deconvolving the fit result with the duration of the pump pulse and the non-collinear geometry yields an effective X-ray pulse length of 140 ± 30 fs FWHM. The timing drifts are below 30 fs rms over 5 days (see Fig. 6). Because spatial and temporal stability are coupled in a grazing incidence geometry, this also implies that the X-ray beam at the sample did not move more than approximately 5 μm during this extended time period.

Femtosecond-level synchronization between the optical laser and the X-ray pulse is needed to extract meaningful data with sub-picosecond time resolution in an XPP experiment. Because the optical pump and X-ray probe pulses are derived from the same Ti:sapphire laser system, the temporal evolution of a system can be traced in ~ 50 fs time steps by delaying the arrival time of the pump pulse relative to the X-ray pulse by using an optical delay line. The source can be stroboscopically operated over

Fig. 5. X-ray pulse length and time resolution: Normalized integrated diffracted intensity from the bulk Bi (111) reflection at 7.15 keV as a function of pump-probe delay for excitation fluence of $1.4 \text{ mJ}/\text{cm}^2$. An effective time resolution of 195 ± 25 fs FWHM including time drifts and a X-ray pulse length 140 ± 30 fs FWHM is extracted from this data. A shift of the fast initial drop in diffraction intensity would indicate a change of time-zero t_0 .

Fig. 6. Timing stability: Time-zero drifts measured during 5 days of consecutive scans (the horizontal error bars indicate the length of the scans). Hence inherent synchronization enables multishot data accumulation for days with timing stability of 30 fs rms.

millions of shots for many hours or even days with effective time resolution ~ 85 fs rms. For samples that exhibit a reproducible, repetitive response to photoexcitation, the low flux of the source is compensated to a certain extent by its long term stability. This allows to perform XPP experiments with ‘traditional’ pump-probe techniques where the data are acquired sequentially in a controlled manner. The timing stability is solely due to the jitter or drift of the travel distances of the laser and X-ray beams. It is not affected by changes in the arrival time of the electrons, although large scale changes will result in fluctuations in the sliced X-ray intensity.

5. Temporal coherent radiation

An ensemble (or bunch) of relativistic electrons occupying a small volume in phase space emits incoherent (ISR) as well as coherent (CSR) synchrotron radiation. Noting from the definition of the Poynting vector that the radiation power is quadratic with respect to the electric charge, a linear or quadratic dependence of the total emitted intensity on the number N_e of the electrons in the bunch is expected, depending on whether the emission of all elec-

trons happens out of phase (ISR) or in phase (CSR) [48]. ISR is present at any wavelength below the critical wavelength λ_c (defined by the vacuum chamber). The value of λ_c is typically in the far-IR spectral range. CSR is observed only when either the entire electron bunch or any longitudinal density modulation within the bunch is equal to or shorter in length compared to the radiation wavelength being emitted. Under this condition the radiation from all electrons is emitted with about the same phase, *i.e.* the radiation is temporally coherent.

Optical interferometry on the CSR signal is used to estimate the pulse length of the energy modulated electron bunch slice. Gated autocorrelation spectra with a Michelson interferometer are recorded for successive round-trips. The detector is a ‘hot electron’ InSb-bolometer with magnetic enhancement to have sufficient spectral responsivity up to wavenumber 60 cm^{-1} (1.8 THz). The shortest center peak width we measure is $185 \pm 35 \text{ fs}$ FWHM, 8 m downstream of the radiator (‘turn 0’) where the $140 \pm 30 \text{ fs}$ FWHM X-rays are generated. Correcting for the bunch lengthening over the 8 m electron flight path, the sliced pulse width for the electrons and X-rays agree within the uncertainty of the measurement. As expected, for successive round-trips 1–4 we observe in Fig. 7 the increase of the center peak width due to the time-of-flight dispersion of the storage ring. By taking a Fourier transform of the measured interferogram we obtain the power spectrum $F(\omega)$ for each turn. Since $F(\omega)$ is again a Fourier transform of the electron charge density distribution [49], it can be calculated by beam dynamic tracking simulations. Starting with the electron momentum distribution due to the laser-electron interaction, the phase space distribution of the electrons is propagated turn-by-turn through all magnetic elements of the storage ring. Due to lattice dispersion the electron density in the vicinity of the energy modulated slice changes steadily as the electron bunch propagates along the storage ring. At the location where the CSR signal is recorded, the maximum value of the power spectrum is calculated (measured) at wavenumber $59.8 (54.5) \text{ cm}^{-1}$ for the shortest pulse length (‘turn 0’) and $6.4 (8.6) \text{ cm}^{-1}$ after one round trip (turn 1). As shown in Fig. 8, the rapid drop of the wavenumber due to the rapid increase of the pulse length after one turn is well reproduced by the simulations [50]. For turns 2–4 discrepancies become noticeable due to the low frequency cut-off ($\lambda_c = 2.1 \text{ cm}^{-1}$) of the vacuum chamber. We conclude that the dynamics of laser-modulated electron bunches in the slicing spectrometer is well understood.

The basic process in a free electron laser is similar to the laser-electron interaction described for laser slicing. Instead of CSR in the far-IR range, in an XFEL coherent radiation in the Angstrom range is generated. Therefore charge density modulation in the Angstrom range (‘microbunching’) has to be achieved. Consider a short ($150\text{--}300 \text{ fs}$ FWHM) electron bunch with charge 1 nC (6×10^9 electrons), energy $6\text{--}15 \text{ GeV}$, energy spread 0.1% rms, and small angular divergence (normalized emittance $\varepsilon_n \sim 1 \text{ } \mu\text{m-mrad}$) propagating down a long undulator (number of periods ~ 3000) generating incoherent (spontaneous) radiation at $1 \text{ } \text{\AA}$ wavelength. In the beginning, without microbunching, all the N_e electrons in the bunch

Fig. 7. Sliced electron bunch length: Gated autocorrelation spectra of coherent far-IR radiation emitted by the slice energy modulated electron bunch, measured with a Michelson interferometer at the THz-diagnostic port. The evolution of the central peak width indicates the pulse lengthening due to lattice dispersion for successive round-trips from sub-ps ($\sim 200 \text{ fs}$ FWHM) pulse length for ‘turn 0’ to 2.3 ps FWHM after 4 turns (for Gaussian modulated bunches these widths would have to be multiplied by 0.7). For longer pulses the model fits (solid red lines) exhibit discrepancies because of wavelength absorption not included by the low-frequency cut-off due to the vacuum chamber.

($N_e \geq 10^9$) can be treated as individually radiating charges with the intensity of the incoherent radiation $\propto N_e$. After complete microbunching, all electrons radiate almost in phase. This leads to an intensity $\propto N_e^2$ and thus to an amplification of many orders of magnitude with respect to the ISR emission.

Charge microbunching is achieved by combining energy modulation and dispersion. Since in an undulator an electron has a velocity component transverse to the undulator axis and parallel to the radiation electric field emitted by the other electrons, there is an energy exchange causing a change of the electron energy (similarly to the laser

Fig. 8. The power spectrum for turn 0–4 is obtained by a Fourier transform of the measured interferograms shown in Fig. 7. The maximum value of the spectrum is plotted and compared to the maximum value calculated by beam dynamics simulations (*i.e.* simulation of the electron momentum distribution after the laser-electron interaction and subsequent tracking of this distribution turn-by-turn through the magnetic elements of the storage ring). Due to the cut-off wavelength of the vacuum chamber corresponding to wave number 2.1 cm^{-1} , longer wavelengths in the measured spectra are suppressed, which leads to higher values compared to calculation for turns ≥ 1 .

energy modulation described in section 3). Over the distance of an undulator period, the trajectory of an electron with larger (smaller) energy than the nominal one are bent less (more). As a result, the electrons get bunched on the length scale of the resonant wavelength λ_r . Hence the electromagnetic field and in turn the energy exchange and bunching increase, resulting in a linear and subsequently exponential growth. Saturation sets in when the number of bunched electrons is in the order of N_e , the total number of electrons in the bunch. At this point the coherent power $\propto N_e^2$ ($N_e \geq 10^9$) is many orders of magnitude with respect to ISR of the undulator. The coupled process of charge microbunching and exponential growth in radiation intensity is called ‘FEL collective instability’.

Incoherent undulator radiation has its origin in the density fluctuations (or shot noise) in the electron beam. The energy radiated by the electron beam therefore should be equal to the number of electrons in the beam times the energy radiated by a single electron. This in accordance with observation. An FEL amplifier starting from shot noise is called a self-amplified spontaneous emission (SASE) FEL. When operating in the linear regime, a FEL amplifier can be considered as a linear filter, which does not change the statistics. As a result, the Gaussian random process of shot noise in the electron beam generates radiation which is also a Gaussian random process. The output intensity therefore is proportional to the initial random bunching of the electron beam at the FEL resonance frequency ω_r . If, as it is the case in SASE, there is no input electromagnetic field at the undulator entrance, radiation is still emitted when the longitudinal charge density distribution of the electron beam is non-uniform, and has a Fourier component $A(\omega_r)$ at $\omega_r = 2\pi c/\lambda_r$. The amplitude of the electromagnetic field is then proportional to $A(\omega_r)$ and the intensity is proportional to $|A(\omega_r)|^2$. For a long undulator, the electromagnetic field grows exponentially along the undulator axis, z , with growth rate $1/L_G$ (L_G : gain length), and the intensity will grow as $I \propto |A(\omega_r)|^2 \exp(2z/L_G)$ until saturation is reached after about 20 gain lengths [20].

A high-gain FEL amplifier amplifies only a narrow frequency band of the initial spectrum. Within one gain length the microbunches amplify the highest field amplitude $A(\omega_r)$. Therefore the radiation emitted by each microbunch as well as the radiation emitted in one gain length is temporal coherent. However, if the fluctuations are such that the phase and magnitude of the highest field amplitude changes from gain length to gain length as in the case of a SASE FEL amplifier, the total radiation pulse will not be temporal coherent but exhibits statistical fluctuations (or ‘spikes’) in energy and time which can be quite unfavourable for certain spectroscopic applications. For the linear regime of FEL operation the number of spikes can be estimated [51]. A single shot spectrum of a radiation pulse of duration τ should contain about $q\omega_r\tau$ radiation spikes with a typical width of about $1/(q\omega_r)$ (the FEL parameter q for soft X-rays is $\sim 3 \times 10^{-3}$ and for hard X-rays $\sim 5 \times 10^{-4}$). When approaching the saturation point, the statistical properties of the radiation change drastically on the scale of one gain length. The fluctuations reduce by a factor of two with respect to the

linear regime. The scaling predicts that for very short pulses ($\tau \sim 10$ fs) in the soft X-ray range the number of radiation spikes should be reduced to almost a single spike. This indeed has been observed at the FLASH facility [52]. To lock the relative phase of the highest field amplitude with respect to the microbunches in order to always amplify the same field over each gain length, a coherent input radiation field (or ‘seed’) is needed which is several times larger in amplitude than the highest random field fluctuation due to shot noise. This way all fluctuations could be suppressed, including the jitter of the ~ 10 fs lasing fraction within the electron bunch due to nonlinear collective effects caused by the longitudinal pulse compression (also observed at FLASH). Laser-seeded high-gain FEL amplifiers are therefore of special interest for XPP experiments in the future (see section 7).

6. XPP diffraction: Peierls-distorted solids and manganites

To develop methods which are sensitive to lattice effects induced by electronic excitation, systems that exhibit structural distortions in or near its groundstate are of primary interest. Several materials (Bi, Sb, As and Te) exhibit a strong Peierls distortion under normal conditions resulting in a significant coupling between valence electrons and atomic structure. Although bismuth, which has frequently played a pioneer role in the history of metal physics [53], is not commonly considered as a strongly interacting electron system, the recent observation of signatures of fractional quantum Hall effect in 3D crystals below 1.5 K demonstrates strong interaction among electrons and their condensation to a many-body quantum state [54]. Its equilibrium unit cell structure is rhombohedral (A-7) [55, 56]. At room temperature, the unit cell consists of two Bi atoms on the body diagonal of the unit cell, separated by a distance that is nearly equivalent to half the length of the diagonal. The Peierls mechanism [57] is responsible for the slight deviation from higher symmetry, and also results in a semimetallic electronic structure [58] exhibiting a double-well interatomic potential [60, 62]. The equilibrium coordinate and shape of the well along the trigonal (111) direction can easily be perturbed by optically exciting carriers from the valence to the conduction band. If the excitation is short compared to the time scale of the atomic motion, the Bi atoms perform a damped oscillation about the new equilibrium position along the body diagonal (A_{1g} mode). Extremely large A_{1g} phonon amplitudes in bismuth induced by an intense fs laser pulse have been measured in a pioneering time-resolved XPP experiment with a laser plasma source [8]. Subsequently, in one of the first accelerator based femtosecond X-ray diffraction experiments, electronic softening of the interatomic potential has been measured [45].

In semimetals we currently investigate laser-induced phonon-phonon interactions and the fluence-, depth- and temperature dependence of coherent phonon relaxation. Provided the source is sufficiently stable, XPP diffraction is sensitive to subtle spatiotemporal changes. To prove this, we recently demonstrated control of optical phonons

during an X-ray diffraction measurement on bismuth [22]. In this double-pump experiment the amplitude of the coherent atomic motion can be manipulated [59] through the delay of a second pulse by keeping the electronic energy density approximately constant [60]. The spectra shown in Fig. 9 are obtained by delaying the second pump pulse over one oscillation period of the coherent optical phonon. Its amplitude is either amplified (Fig. 9b) or suppressed (Fig. 9c), depending on the relative delay of the second pulse with respect to the coherent phonon generated by the first pulse. The simulated curves are obtained by assuming a linear dependence on laser fluence to calculate the fractional electron-hole pair density $n(t)$ (as a fraction of the total number of valence electrons). The atomic motion $z(t)$ along the (111) direction is described as a damped harmonic oscillation due to the interatomic potential $V(n(t), z)$ published in Ref. [60, 61]. Density functional theory (DFT) calculations predict that at high laser excitation fluence not only the A_{1g} phonon mode, but also the E_g mode corresponding to an atomic motion in the plane perpendicular to the (111) body diagonal could be excited, as well as coherent coupling between them [62]. So far this topic has been investigated by femtosecond optical reflectivity measurements [63]. Double-pulse XPP experiments will allow us to measure the diffraction from planes orthogonal to (111) when the A_{1g} oscillation amplitude is either amplified or suppressed. Coherent phonon coupling therefore can directly be studied as a function of laser fluence and sample temperature.

In manganites, transition metal (TM) oxides with perovskite-type structure, temperature dependent orbital and charge order transitions occur, which have extensively been studied in the past (see [64] and references therein).

Fig. 9. Measured (symbols) and simulated (solid curves) bismuth (111) coherent optical phonon oscillation controlled by a 2-pulse excitation scheme. The absorbed energy density per pulse was 1.12 mJ/cm^2 . Right axis: atomic displacement as inferred from the simulation.

To address the question about the fundamental time scale of the coupling of such transitions to structural changes, we plan optically excited XPP diffraction studies on the three dimensional $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \sim 0.5$) system. Whereas for low doping ($x < 0.5$) this system undergoes an insulator-metal transition with a ferromagnetic ground-state, for high doping ($x \geq 0.5$) it displays orbital order (OO) and charge order (CO) below the charge-ordering temperature T_{CO} with an antiferromagnetic ground-state [65–67]. Using femtosecond optical pump-probe spectroscopy, a strong coupling of coherent optical and acoustic phonon generation in half doped $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5, 0.58$) due to the charge-ordering transition has recently been observed [68]. By laser induced XPP experiments on this compound at the FEMTO source, the change in amplitude, in frequency, and the dephasing of coherent phonons with oscillation period $\sim 450 \text{ fs}$ in the vicinity of the charge-ordering temperature $T_{\text{CO}} \sim 180 \text{ K}$ can be measured. This will allow us to characterize the strong coupling of the oscillation to the underlying photo-induced charge-ordering phase transition (where electrons are excited from the Mn^{3+} to Mn^{4+} sites) to provide relevant information as to what is responsible for this strong correlation between the lattice and the charge order of the system. In particular we can investigate the possibility of inducing a metal-insulator transition by a mode selective vibrational excitation. For the first time, this process has recently been demonstrated in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, namely a 10^5 drop in resistivity associated with a non-equilibrium transition from the stable insulating phase to a metastable metallic phase by vibrationally driven large amplitude Mn-O distortions (phonons) when the solid resides in its electronic ground state [69].

For the half doped layered $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ system such experiments can be applied to the Mn K -edge [70] in the hard X-ray regime by directly probing the Mn $4p$ states. These experiments are believed to be sensitive to the Jahn-Teller distortion [71]. In the soft X-ray regime, the Mn $L_{2,3}$ edges provide direct sensitivity to the Mn $3d$ states [72, 73], and the oxygen K -edge is sensitive to oxygen $2p$ states [74]. To address the question on which time scale orbital, charge and lattice order-disorder phenomena happen, $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ may be a particular interesting case to apply time-resolved RXD. For this system a temperature dependence for the orbital sensitive superlattice reflection has been observed with resonant soft X-ray scattering (RESOXS) which is different from the temperature dependence measured for the Jahn-Teller distortion [75]. A possible explanation could be the different time scales which govern the underlying fluctuations. Again, characteristic changes in amplitude, frequency and dephasing of coherent phonons at THz frequencies below and above the transition temperature $T_{\text{CO}} = T_{\text{OO}} \sim 240 \text{ K}$ should provide a first answer on the relevant time scales. When probed separately, it will also be interesting to see how different electronic shells respond at very short times. Such RXD experiments rely on the measurement of superlattice reflections, which can be quite weak. They can not be done at a low flux slicing facility, but will become feasible both at soft X-ray FELs and future hard X-ray XFELs. By exploiting the 3rd harmonic lasing of the FLASH free

electron laser providing 10^9 photons/pulse, time-resolved RXD at the oxygen *K*-edge (530 eV) and the manganese $L_{2,3}$ edges (640 eV and 655 eV) are planned in the near future. X-ray pulses as short as 10 fs have already been demonstrated [52]. The minimum time resolution therefore will mainly depend on the accuracy by which the arrival of the X-ray pulses can be controlled and measured.

In addition, polarization analysis of the incoming and scattered X-rays will allow to interpret RXD experiments in terms of electromagnetic multipoles to characterize phase transitions by the symmetry of its order parameters. The polarization analysis of the diffracted beam can resolve resonances determined by multipolar tensors of different order that are very close in energy, exploiting their different relative phase shifts [76]. Therefore time-resolved RXD and polarization measurements will have to be combined, where azimuthal-angle (Ψ) scans (by sample rotation about the Bragg vector) as well as polarization analysis of the scattered beam are performed. The linear polarization of the incoming beam is rotated from horizontal (π) to vertical (σ) (using a polarized undulator in the case of soft X-rays and diamond phase plates in the case of hard X-rays, respectively). Polarization analysis of the scattered radiation is performed for hard X-rays with appropriate analyzer crystals [77] and for soft X-rays with a multilayer analyzer. Horizontal and vertical positioning of the analyzer allows for π' and σ' detection of the scattered X-rays [78, 79].

7. XPP diffraction: seeded free electron lasers

XFEL sources presently under construction [19–21] are based on self-amplified spontaneous emission (SASE). They will provide transverse fully coherent, short X-ray pulses of length 150–250 fs FWHM (using magnetic pulse compression) and intensity 10^{12} ph/pulse at 1 Å wavelength. Depending on the repetition rate, the average flux will be 10^{14} – 10^{16} ph/s in a 0.1% bandwidth, 10 orders of magnitude higher compared to the flux reported in this paper. New kinds of femtosecond X-ray diffraction experiments, such as XPP coherent scattering [80, 82, 83], XPP diffraction on dilute samples [84, 85], resonant magnetic scattering [86], and non-linear X-ray diffraction, will become possible. To perform such experiments, longterm spatiotemporal stability despite the high flux may still be needed once split pulse techniques (transmission 10^{-3}), pulse slicing techniques (efficiency $\sim 10^{-2}$), polarization studies using phase retarders (transmission 10^{-1}) or non-linear X-ray processes (efficiency 10^{-5} – 10^{-11}) are employed.

Nonlinear X-ray physics is a virtually unexplored area because X-ray lasers have not been available. Current ultrafast (linear) XPP diffraction probes the ground-state charge density and yields information about the atom cores. Hence we can see atomic motion, but how the valence charge density evolves is not directly measurable. Understanding the evolution of atomic scale valence charge distortions is of fundamental interest. Optical-X-ray mixing (efficiency: 10^{-5}) probes the excited states responsible for the microscopic charge distribution [87]. This

two-color wave mixing process can be thought of as X-rays which are inelastically scattered off the optically driven valence charge oscillations. The optical-X-ray mixing efficiency therefore probes solely the valence charge density with atomic spatial resolution. It is a direct measure of these local distortions and can provide information on coupling (dipole-dipole) between local distortions in condensed matter. Furthermore, by tuning the X-rays to a core valence resonance, nonlinear RXD may allow a view of valence charge distortions in an element specific manner.

Several schemes have been proposed to generate very short X-ray pulses (0.4–100 fs, depending on the scheme) at FELs (for an overview see [88, 89], and references therein). To perform XPP experiments in a controlled manner by exploiting inherent synchronization similar to Fig. 1, laser seeding is again a promising technique, but challenging. To overlap with the central area of the electron bunch, it requires a synchronization of the femtosecond laser pulse to the electron bunch within a fraction of the electron bunch duration (~ 30 fs rms) [19]. Furthermore, the laser manipulation must not degrade the FEL gain. The high-gain harmonic generation (HGHG) FEL has been proposed in the early 1990s [29] to generate fully coherent, transform limited UV pulses. HGHG can be used to generate radiation pulses with < 20 fs duration. It relies on an optical seed laser (Ti:sapphire at 800 nm, or a higher harmonic generated in a nonlinear crystal or a gas) at subharmonic wavelength. The energy modulation imposed on the electron beam in the modulator by the seed laser is converted to a coherent spatial charge density modulation in a subsequent dispersive section. The radiator, tuned to a higher frequency of the seed laser, causes the microbunched electron beam to emit fully coherent radiation at that harmonic frequency. Operated as an amplifier seeded by coherent radiation, HGHG therefore can overcome the intrinsic noise of the SASE radiation. Single-stage HGHGs at IR and UV wavelengths have been demonstrated [90, 91]. In principle the HGHG FEL can be cascaded to reach still-shorter wavelengths. Several facilities have been proposed in the soft X-ray spectral range (0.1–1 keV) [92] and one, FERMI@Elettra, is under construction.

To generate < 10 fs hard X-rays in the Angstrom wavelength regime, two seeding schemes are under intense theoretical study: (i) generation of sub-fs (attosecond) pulses from energy-modulated electron bunches in a X-ray SASE FEL by a high-power (~ 1 TW), carrier-envelope phase stabilized, few cycle laser (5–7 fs) in a 2-period modulator [19, 93–96]; and (ii) seeding by high order harmonic generation (HHG) generated by ultrashort optical laser pulses in a gas target to produce fully coherent hard X-ray FEL emission with tens of fs duration [97]. In the case of few-cycle energy modulation, the laser driven local electron energy chirp produces a correlated frequency chirp of the resonant radiation in the undulator $\delta\omega/\omega = 2\delta\gamma/\gamma$. Because the central peak electron energy modulation ($\Delta E/E = 2 \times 10^{-3}$) is largest and in particular larger than the FEL bandwidth ($\delta E/E \sim 10^{-3}$), the FEL undulator can be tuned such that it amplifies only within a small fraction of the optical cycle. This way sliced sub-fs X-ray

pulses are produced. There is a concern that the local energy chirp can be sufficiently large to act like an effective energy spread to degrade the FEL gain. However, as pointed out recently [96], as long as the associated local energy chirp is linear, it could be compensated perfectly by a proper magnetic taper of the undulator (*i.e.* slowly reducing the undulator field strength to preserve the resonance wavelength as the longitudinal kinetic energy of the electron increases). Thus a tapered undulator can automatically ‘select’ a slice fraction of an energy-modulated bunch that has the right energy chirp to generate high power (up to tens of Gigawatts), sub-fs X-ray pulses. In this case the effect of monochromatization on the pulse duration in a crystal has to be taken into account. The time needed for the pulse to traverse an extinction depth D_e is $t = \pi D_e \sin(\theta)/c$ in the case of perfect crystals. The smaller the grazing angle of incidence, the smaller is the response time for a given Bragg reflection. For XFEL radiation at 12.4 keV incident under 0.5° on a Si crystal with $D_e \sim 30 \mu\text{m}$, a pulse broadening of $\Delta t \simeq 3 \text{ fs}$ is estimated. For X-ray pulses below 10 fs this effect cannot be neglected.

Complementary to inherent synchronization based on laser seeding, the pump-probe timing could be measured for every pulse pair to time-stamp and group each scattering event in a non-sequential manner. However unlike optical pulses, there is no standard diagnostic method to characterize the pulse length and timing stability of femtosecond hard X-ray pulses in a single shot. In particular, an optical-X-ray cross-correlation method which is non-destructive to the X-ray beam and which has sufficient temporal resolution and a large signal-to-noise ratio has yet to be realized for hard X-rays. For XPP experiments at SASE FELs, such a diagnostics is needed. Furthermore, anticipating a XFEL pulse length below 10 fs (similar to what has already been achieved for soft X-rays at the FLASH facility at DESY [52]), the timing control and resolution required may be achieved only by combining both methods, namely active synchronization and single-shot time-stamping measurements. A first step towards non-sequential time-stamping XPP measurements has been demonstrated at the Sub-Picosecond Pulse Source (SPPS) at SLAC. Employing an electro-optical (EO) technique [26] that measured the relative timing of a femtosecond optical laser with respect to the electron bunches (optical laser and electron bunch cross-correlation), a short-term time resolution of 60 fs rms in a XPP experiment has been achieved which allowed a post-sorting of time stamped laser-X-ray pump-probe data [45]. In this case, multishot data acquisition was done within 20 minutes. The EO-technique measures the change of polarization of a laser when it crosses a birefringent crystal (ZnTe or GaP) in the presence of a large electric field pulse induced by the short electron bunch. Similar to Fig. 5, due to transverse optical phonon excitation at 5.3 (11) THz in the ZnTe (GaP) crystal, this method will be limited to a time resolution of ~ 80 (40) fs rms respectively. Therefore, to ideally measure the arrival time of the X-ray pulses (instead of the electrons) in the range 1–10 fs, new cross-correlation methods will have to be developed. A promising concept for this purpose is the measurement of the

final kinetic energy of X-ray generated photoelectrons in the presence of an oscillating light field at the instant of ionization [98–100] or the measurement of the X-ray-pulse induced transient changes of the optical reflectivity in semiconductors [101].

8. Summary and conclusions

Today most results on structural dynamics with atomic spatial resolution and sub-ps time resolution in the range 200–500 fs FWHM have been obtained by pump-probe X-ray and electron diffraction experiments using table-top laser based sources. In contrast, undulator sources where such experiments can be performed are mostly still under development. We have presented the performance of a low flux undulator source that produces tunable, incoherent X-rays in the $1 \text{ \AA}$ wavelength range with pulse length $140 \pm 30 \text{ fs}$ FWHM. Operated at a highly stable storage ring and exploiting inherent synchronization due to laser slicing, multi-shot laser-pump and X-ray-probe experiments with timing stability 70 fs FWHM and instrumental time resolution 200 fs FWHM can be performed over an extended time period of several days. The spatiotemporal stability needed for grazing incidence diffraction has been demonstrated by control of coherent optical phonons. We conclude that laser manipulation of the phase space density of relativistic electrons in a periodic undulator field is a proven technique to generate 100 fs X-rays in a controlled way. Due to the development of appropriate diagnostics, laser slicing is now well understood both in the electron and the X-ray channel. The next frontier will be a time resolution of 10 fs or below. At the FLASH facility it has already been demonstrated that a soft X-ray SASE FEL can generate 10 fs rms pulses in the range 90–450 eV with 10^9 – 10^{12} photons/pulse in a 0.1% bandwidth. A similar performance is anticipated at $1 \text{ \AA}$ once the XFEL facilities now under construction started operation. To overcome the noisy pulse structure and the fluctuating arrival time of SASE X-ray pulses, laser seeding may be a viable option. In case of amplification to generate coherent radiation, the laser-electron interaction and the FEL operation of the undulator become even more intricate compared to laser slicing. Laser slicing therefore can be considered as an intermediate step towards laser seeded FEL amplifiers to perform XPP experiments in a controlled manner with ever shorter pump and probe beams of high peak intensity. Nonetheless, successful experiments will have to rely on single-shot cross-correlation diagnostics between the optical laser and the FEL pulses without destroying the X-ray beam. For hard X-rays such a diagnostic does not yet exist. Once developed, it has to allow the post-sorting of time-stamped XPP data in a non-sequential manner to achieve a time resolution below 10 fs in combination with active synchronization. Not surprising, femtosecond time-resolved X-ray techniques will merge with other experimental X-ray methods developed for static measurements over many years. We have discussed the combination of time-resolved X-ray pump-probe diffraction and resonant X-ray scattering techniques which is of relevance for our work. Time-resolved RXD

will be a technique well suited to study both the structural and electronic stimulated coherent dynamics in complex materials during phase transitions or ordering processes. Polarization analysis will allow to characterize phase transitions by the symmetry of its order parameters. Once the sub-ps structural dynamics has been measured at the SLS FEMTO facility and the static electronic ordering at the SLS RESOXS station for the same complex systems, we subsequently plan time-resolved RXD experiments at the FLASH soft X-ray laser to reveal the correlated structural and electronic dynamics as they develop. At future XFELs, XPP diffraction experiments will be an important class of time-resolved experiments. Only shortly mentioned, there are other important areas where ultrafast X-ray diffraction is rapidly advancing. Coherent diffraction imaging and liquid phase time-resolved X-ray diffraction are two prominent examples where the study of femtosecond dynamics in nanoscale biological and chemical samples most likely will profit from the approach presented in this paper.

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