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Time-resolved x-ray photoelectron spectroscopy at FLASH

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Abstract. The technique of time-resolved pump–probe x-ray photoelectron spectroscopy using the free-electron laser in Hamburg (FLASH) is described in detail. Particular foci lie on the macrobunch resolving detection scheme, the role of vacuum space-charge effects and the synchronization of pump and probe lasers. In an exemplary case study, the complete Ta 4f core-level dynamics in the layered charge-density-wave (CDW) compound 17°-TaS\textsubscript{2} in response to impulsive optical excitation is measured on the sub-picosecond to nanosecond timescale. The observed multi-component dynamics is related to the intrinsic melting and reformation of the CDW as well as to extrinsic pump-laser-induced vacuum space-charge effects.

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1. Introduction

Photoelectron spectroscopy (PES) is at present one of the most powerful tools for studying the electronic structure of condensed matter [1]. The backbone of the technique is Einstein’s explanation of the photoelectric effect, in which the quanta of monochromatic electromagnetic radiation (photons) induce electron emission from a solid surface into the vacuum, provided that the photon energy is larger than the work function of the sample [2]. If the photon energy is high enough, photoemission can principally occur from all occupied electronic states near the surface, from the deepest-lying core levels to the highest-lying valence electrons at the Fermi level, and the measured electron energy distribution curve will directly reflect the occupied electronic energy level structure of excited quasi-particle states in the sample. Remarkably, at sufficiently high or low photon energies, also the extreme surface sensitivity of PES becomes somewhat relaxed [3–5].

PES is, in fact, a diverse family of techniques. In the basic experimental scheme, primarily used in x-ray photoelectron spectroscopy (XPS), only one degree of freedom of the emitted electrons is measured at fixed photon energy, namely their kinetic energy. The obtained spectra then provide detailed chemical information with elemental and atomic-site selectivity in the core level regime [6, 7] as well as a direct image of the density of valence electronic states near the Fermi level [8, 9]. In more ambitious schemes, the photon energy is varied and the polar and azimuthal emission angles as two further photoelectron degrees of freedom are measured in addition to the kinetic energy. The corresponding techniques often rely heavily on the use of synchrotron radiation and are called x-ray photoelectron diffraction (XPD) and angle-resolved photoelectron spectroscopy (ARPES) for the core and valence electron regime, respectively. While XPD has played a prominent role in the elucidation of surface atomic structures in real
space [10], ARPES has indeed become the standard technique to map the occupied part of the band structure, including the Fermi surface, in momentum space [11]. Moreover, at the highest energy and angle (momentum) resolutions, ARPES can reveal subtle lifetime effects encoded in the measured line widths and shapes as well as fine details in the band dispersions near the Fermi level, in particular kinks and gaps due to many-body interaction effects [12].

What all these different PES techniques have in common, however, is that they provide time-averaged electronic structure information only. The widths and shapes of the measured spectral lines reflect the average electron dynamics which generally results from an intricate mixture of different types of interactions and fluctuations involving the electronic degrees of freedom. The great appeal of time-resolved spectroscopy techniques, and time-resolved PES techniques in particular, is that they provide, in principle, direct access to the electron dynamics at the timescale of elementary electronic processes and thus may help in disentangling the various processes in the time domain [13]. In fact, this capability has already proven useful in studying non-equilibrium phenomena in condensed matter such as photo-induced phase transitions in complex materials [14] or chemical reactions at surfaces [15, 16].

The probably most effective scheme for time-resolved measurements uses two ultrashort (sub-picosecond) pulses: one to ‘pump’ the system out of equilibrium and the other to ‘probe’ the relaxation back into equilibrium after specified time delays. Using this pump–probe approach, specifically to study ultrafast dynamics of complex materials, x-ray [17] and electron [18] diffraction as well as optical reflectivity [19, 20] and PES [21–25] have successfully been carried to the time domain.

At present, time-resolved pump–probe ARPES can be performed reliably with high precision using near-ultraviolet (NUV) probe pulses [21, 22] created by Ti:sapphire lasers and fourth-harmonic generation in nonlinear optical media [26]. Typical setups routinely deliver sufficiently intense femtosecond pulses with repetition rates of a few hundred kHz. However, the photon energies in the NUV lead to limited access of energy and momentum space, restricted to regions close to the Fermi level near zero momentum. Although higher-harmonics generation (HHG) sources have since relatively early been known to extend the photon energy range significantly towards higher energies [27, 28], practical time-resolved ARPES measurements using HHG sources—and thus allowing access to electron states at the boundaries of typical Brillouin zones—have only very recently become possible [24, 25]. However, these sources still fail to produce sufficient flux for solid-state photoemission experiments for photon energies above 100 eV [29] and they are not easily tunable. Femtosecond slicing represents an alternative way of producing tunable soft x-ray pulses with pulse lengths down to about 100 fs [30, 31]. In this approach, the ultrashort pulses of a Ti:sapphire laser are used to slice certain parts of the typically much longer electron bunches of a third-generation synchrotron radiation source. However, the typical photon energy range starts at about 250 eV and the photon flux is even smaller than what can presently be achieved with HHG sources [32]. To realize the full potential of time-resolved PES, including time-resolved XPS (trXPS) in particular, one needs a light source that generates femtosecond pulses with a tunable photon energy in the extreme ultraviolet (XUV) to soft x-ray regime. Free-electron lasers (FELs) representing the fourth generation of synchrotron radiation sources are such sources [33].

Here, our aim is to give a detailed account of the challenges and prospects of trXPS using the free electron laser at Hamburg (FLASH) [34, 35]. To this end, we have divided the paper into two main parts. In the first part (section 2), we discuss and solve specific experimental issues that are connected with FLASH being a fluctuating high-intensity source with a low repetition...
rate. These are, in particular, photoemission data acquisition, vacuum space-charge effects and synchronization of the optical pump laser and FLASH. In the second part (section 3), we present a trXPS case study on the layered charge-density-wave (CDW) material $1T$-TaS$_2$, in which we extend our previous work [23] in that we reveal the full atomic-site-specific charge-order dynamics after impulsive excitation up to the nanosecond timescale. In particular, we find that the long-term dynamics observed in the Ta 4f core-level spectra has an extrinsic and an intrinsic component. Both components are reasonably explained by an $N$-body space-charge dynamics simulation and a one-dimensional (1D) heat conduction model, respectively. Finally (section 4), we summarize the major conclusions and give a glimpse of the potential role of trXPS in the investigation of ultrafast dynamics in condensed matter with full elemental, chemical and atomic-site selectivity.

2. Experimental background: time-resolved photoemission at the free-electron laser in Hamburg (FLASH)

2.1. The free-electron laser (FEL) FLASH

Starting operation in 2005 and thereby verifying the principle of self-amplified spontaneous emission (SASE) [36], FLASH was the first FEL reaching into the XUV and soft x-ray regime [34, 35]. Currently, FLASH routinely produces bright coherent ultrashort pulses with a fundamental photon energy between 26 and 300 eV, pulse energies up to 130 $\mu$J and pulse durations of 30–150 fs.$^8$

Because of its unique characteristics, FLASH has immediately become a very powerful tool of scientific research, in particular in the study of nonlinear effects in atoms, molecules and clusters and for diffraction imaging of nanostructures and biological samples [37]. Three selected examples of novel results in condensed matter physics are that aluminum becomes transiently transparent under intense XUV FEL radiation [38], that silicon undergoes a liquid–liquid phase transition after intense optical excitation [39] and that magnetic diffraction patterns of a Co/Pt multilayer sample can be obtained in a single shot [40].

All three experiments relied on the detection of photons and thus avoided the problem of vacuum space-charge effects that has commonly been regarded as an insurmountable obstacle to electron spectroscopy measurements at FELs. However, after first measurements on tungsten demonstrated the general feasibility of time-resolved PES using FEL radiation [41], a recent proof-of-principle experiment on the layered CDW reference material $1T$-TaS$_2$ established trXPS as a completely viable technique at FELs [23].

In the following, we will describe in detail how trXPS measurements can be successfully carried out at the monochromator beamline PG2 of FLASH.

2.2. Monochromator beamline and experimental setup

Figure 1 shows the schematic layout of the plane grating monochromator beamline PG2 [42, 43] and the photoemission endstation used in the experiments reported here. In the very beginning, electron bunch patterns are generated by a radio-frequency gun according to the mode of operation of FLASH chosen by the user. In the single-bunch mode, the bunch pattern is made up of single-electron bunches repeated at a rate of a few Hz. In the macrobunch mode, on the

$^8$ FLASH parameters in October 2011. Online at http://flash.desy.de
Figure 1. Schematic overview of the experimental setup at FLASH. The FEL pulses are generated within a 30 m long undulator (a typical bunch pattern, as used in the experiments reported here, is indicated). The gas monitor detector (GMD) and the gas attenuator are tools in the beam path for measuring and tuning FEL pulse intensities. The FEL light is monochromatized by a plane grating monochromator, followed by an additional intensity measurement with the multi-channel plate (MCP) tool. The monochromatic FEL light then passes the collinear laser integration, where the expanded and refocused optical laser is reflected on a mirror with a drill hole for the FEL beam (see inset). Both beams enter the UHV main chamber collinearly and hit the sample mounted on the manipulator cryostat. The emitted photoelectrons are finally detected by a hemispherical spectrometer. The inset shows the laser board with the delay-stage and the photodiodes used to find the temporal overlap between the FEL and pump laser pulses.

other hand, pulse trains, again repeated at a few Hz, consist of up to a few hundreds of single bunches with a bunch-to-bunch separation of a few microseconds [34], as sketched in figure 1.

The electron bunches are compressed longitudinally in magnetic chicanes and accelerated to 1.25 GeV in a linear accelerator, before they enter a long line of fixed-gap undulators where they generate the FEL radiation via the SASE process and are dumped at the end. Due to the stochastic nature of the SASE process, every photon pulse has different characteristics making FLASH a fluctuating source. For this reason, the facility provides several tools to monitor the intensity of the generated FEL radiation parasitically with single-pulse resolution [45–48]. For example, the gas monitor detectors (GMDs), which are positioned at both ends of the 15 m long gas attenuator, are based on the photoionization of rare gases and subsequent measurement of the photocurrent. The gas attenuator can be used to weaken the pulse intensity by several orders of magnitude without altering other FEL beam characteristics. Figure 2(a) shows a typical FEL
intensity measurement that was recorded with a GMD placed in front of the gas attenuator. The plotted curve reveals intensity drifts of up to 50% on a timescale of about 30 min.

Compared to third-generation synchrotron radiation sources, the spectral resolution of the radiation at the end of the line of undulators is rather high \( (E/\Delta E \approx 100) \). This is because the effective undulator length is significantly longer (30 m) in order to achieve saturation of the SASE process. While this level of monochromatization is already sufficient for many types of experiments, high-resolution PES measurements typically require spectral resolutions of 1000–50 000. The plane grating monochromator at the beamline PG2 of FLASH allows the user to choose between a high-resolution and a high-transmission mode using gratings with 1200 and 200 lines mm\(^{-1}\), respectively. The theoretical resolving power can be varied from roughly 4000 to 70 000 [42]; however, the experimentally achieved resolution is about a factor of two lower [44]. The monochromatization in a plane grating geometry necessarily changes the temporal characteristics of the FEL pulses. The spread of the optical path lengths increases with the number of illuminated lines on the grating, thus giving rise to a temporal stretching of the pulses [44]. For example, if the monochromator with the 200 lines mm\(^{-1}\) grating is set to 50 meV spectral resolution, the minimum pulse length becomes \( \sim 83 \) fs [49]. In particular, regarding time-resolved PES measurements, this reinforces the need to find a reasonable trade-off between spectral and temporal resolution.

Aside from the long-term intensity drifts on the timescale of several minutes, the FEL radiation produced by FLASH also shows pulse-to-pulse fluctuations in intensity and energy within each macrobunch. These short-term fluctuations are detected with MCP tools by reflecting a small part of the incoming photons via a gold mesh to an MCP and measuring its discharge. Figure 2(b) shows typical pulse-to-pulse fluctuations within an exemplary macrobunch consisting of 30 pulses as recorded behind the monochromator. Intensity...
fluctuations are generally increased by the monochromator because it translates the energy fluctuations within each pulse into additional intensity fluctuations.

In addition to an accurate shot-to-shot characterization of the FEL pulses before they hit the sample, a time-resolved pump–probe photoemission experiment at FLASH requires the integration of a pump laser. At the facility, an optical laser system provides pump pulses with a fundamental wavelength of 800 nm, a duration of about 120 fs and an energy of up to 60 µJ [50, 51]. The laser system is able to mimic the pulse pattern of the FEL in the macrobunch mode with up to 8000 pulses per second. However, when two independent short-pulsed light sources are used, spatial and temporal alignments become challenging. Our most practical solution is a collinear laser integration located between the monochromator and the main experimental chamber (see the inset of figure 1). The central part is a plane mirror, with a diameter of 50 mm and a drill hole of 2 mm, which is tilted by 45° with respect to the FEL beam. The optical laser beam is expanded by a telescope before passing a focusing lens to minimize intensity losses by the mirror drill hole. The mirror reflects the optical beam collinearly with the FEL beam, which passes through the drill hole, onto the sample.

In our experimental setup, the samples are mounted on a liquid-helium-cooled cryostat and placed in the center of a µ-metal shielded ultrahigh vacuum (UHV) chamber, in which the photoemission measurements are carried out at a base pressure of ∼3 × 10⁻¹⁰ mbar. The emitted photoelectrons are detected by a hemispherical electron analyzer (VG Scienta SES 2002) using a charge coupled device (CCD) detection scheme consisting of a stack of MCPs, a phosphor screen and a Basler 102F CCD camera.

2.3. Photoemission data acquisition

Our photoemission experiments were performed in March 2009 before a major upgrade of FLASH. We utilized the macrobunch mode at a master frequency of 5 Hz with each macrobunch consisting of 30 FEL pulses repeated at a period of 4 µs.

During photoemission measurements, the CCD detector images were stored at the master frequency and marked with the characteristic timestamp provided by the facility. Each CCD image therefore represents an average over one macrobunch and can be linked to the corresponding FEL pulse properties, as all instruments of the facility, for example the previously mentioned GMD and MCP tools, save their data with the same timestamp. In the employed CCD detection scheme, a single-shot measurement at the 250 kHz single-pulse repetition rate in the macrobunch mode is currently not possible because of the slow CCD readout time.

A typical CCD image is depicted in figure 3(a) showing about 20 detector hits (in the following called ‘blobs’) spread around the central horizontal axis. In this case, the analyzer was operated in the so-called transmission mode, in which the horizontal axis is the energy dispersive direction and the vertical axis represents spatial position along one direction on the sample. Since in our experiments the sample surface is typically large and homogeneous, the spatial information can be conveniently used to align the FEL beam spot on the sample to the focus of the entrance lens of the photoelectron spectrometer.

After the measurements, an acquired stack of CCD images is analyzed in two steps. Firstly, the center-of-mass position of every blob above a pre-selected intensity threshold is determined. Secondly, the obtained blob positions are accumulated into a histogram by integrating over the space axis and over pre-specified intervals along the energy axis. Figure 3(b) shows an exemplary Ta 4f core-level spectrum of 17-TaS₂ as emerging during data analysis.
Figure 3. (a) Typical CCD image of the phosphor screen in the exit plane of the hemispherical electron analyzer. The image shows 20 detector hits (‘blobs’) and represents an average over the 30 pulses of one macrobunch. It was recorded in the transmission mode of the electron analyzer at a central kinetic energy of 127 eV, a pass energy of 50 eV, an analyzer slit width of 1.5 mm and a resulting energy resolution of 285 meV. The horizontal axis is the energy dispersive direction, while the vertical axis represents the spatial position on the sample. (b) Intensity histogram illustrating a typical energy binning and the accumulation of a Ta 4f core-level spectrum of $1T$-TaS$_2$ from several thousand CCD images.

The chosen approach not only leads to a high signal-to-noise ratio but also allows for an efficient handling and sorting of the acquired data. The latter is particularly required in order to deal with the unpredictable intensity fluctuations of the FEL radiation that can cause a significant degradation of the accumulated spectra via vacuum space-charge effects.

2.4. FEL-induced vacuum space-charge effects

Vacuum space-charge effects are arguably the most important limitation for PES at FELs and other intense and short-pulsed sources. Unfortunately, they turn FLASH’s unique feature of extremely high peak brilliance into an experimental challenge: the FEL pulses will generate a dense cloud of photoelectrons in front of the sample surface such that the Coulomb repulsion between the emitted electrons will strongly distort the initial energy distribution on the way from the sample to the detector. In particular, peaks in the spectra will be shifted and broadened [41, 52–56], which can result in a dramatic loss of the effective energy resolution. In general, these space-charge effects tend to increase with increasing the number of electrons per pulse and decreasing the pulse duration and spot size on the sample [52].
To investigate the role of FEL-induced space-charge effects in our trXPS experiments, we have carried out (time-averaged) PES measurements on the CDW split Ta 4f\textsubscript{7/2} core level of 1\textit{T-TaS}\textsubscript{2} [57] over a range of FLASH intensities. Note that in the analysis of the data we can use the number of blobs per CCD detector image as a convenient measure of the macrobunch-averaged FEL intensity at the position of the sample. Figure 4(a) shows how the spectra evolve when they are accumulated from different blobs-per-image intervals with an increasing average intensity (gray bars in figure 4(b)). Clearly, with increasing the average number of blobs per detector image, the Ta 4f\textsubscript{7/2} doublets are shifted to higher kinetic energies (lower binding energies), the peak-to-valley ratio decreases and the right edge of the spectrum is smeared.
To quantify the observed effects, we have fitted all Ta 4f$^{7/2}$ spectra with a model function consisting of two Doniach–Šunjić lines (plus a linear background) convolved with a Gaussian and have used the fitted peak position and Gaussian full-width at half-maximum (FWHM) (after correcting for the ‘intrinsic’ width of 285 meV) as a measure of the spectral shift and broadening, respectively. Figure 4(c) shows the results as a function of the average number of blobs per detector image. Both the spectral shift and the broadening increase linearly and reach values of up to 220 and 350 meV, respectively, at the highest applied intensity of 60 blobs per image. Remarkably, even at the supposedly low FEL intensity of 10 blobs per image the spectral shift is already considerable (about 50 meV). Note that the absolute energy scale of all Ta 4f core levels shown here was calibrated using high-resolution synchrotron data.

To verify that the intensity-dependent spectral shift and broadening are due to vacuum space charge, we have performed a molecular dynamics simulation based on the relevant experimental parameters, namely the spatial and temporal profile of the FEL pulses and the photoemission geometry. For simplicity, the undistorted spectrum was assumed to be a single Gaussian of 285 meV FWHM sitting on a constant background (see [52] for details of the simulation). The results are plotted in figure 4(c) and confirm the experimentally observed linear dependence of the energy shift and broadening on the number of emitted electrons per macrbunch. The clear correlation between the results of the experiment and the simulation allows us to estimate that for our experimental parameters 1 blob per pulse on the detector image corresponds to about 30 000 photoelectrons per pulse emitted into the hemisphere.

The results of the simulation corroborate that it is essential to think about space-charge effects before FEL photoemission experiments are done. At FLASH before the upgrade in 2009, typical FEL pulses had a duration $\tau_{FEL}$ between 10 and 70 fs and were stretched by the monochromator at the beamline PG2 to about 100 fs. The spot diameter $d_{FEL}$, on the other hand, was about 50 $\mu$m in the focus of the beamline. Thus, with a typical speed of the electrons perpendicular to the sample surface $v_e = 6.5 \times 10^{-3} \mu$m fs$^{-1}$ corresponding to a kinetic energy of 120 eV, we have $v_e \tau_{FEL} \ll d_{FEL}$ and the initial shape of the emitted photoelectron cloud becomes a flat disc. In this regime, space-charge effects are known to be almost independent of the pulse duration and to be inversely proportional to the spot diameter [52]. Hence, to minimize spectral deterioration, we moved the experiment 50 cm out of focus, widening the spot diameter on the sample to about 500 $\mu$m (at a typical sample size of $4 \times 4$ mm$^2$). In this geometry, it was possible to control the number of emitted electrons per FEL pulse via the gas attenuator over a sufficiently wide intensity range without losing too much spectral resolution due to space charging. Note that we employed the third FEL harmonic whose intensity is typically two orders of magnitude lower than the intensity of the fundamental.

In the end, choosing a reasonable trade-off between statistics and effective resolution, we have performed the reported experiments in an average FEL intensity regime corresponding to 20–30 blobs per detector image and discarded all images containing more than 30 blobs from the analysis. The space-charge-induced energy shifts and broadenings were thus limited to about 100 and 150 meV, respectively (see figure 4(c)), and the typical measurement time per core-level spectrum was about 3 min.

### 2.5. Synchronization of the FEL and the pump laser

While the experimental challenges discussed in the previous two sections were specific to the method of PES, the challenge discussed now is a general one concerning all pump–probe experiments at FLASH that employ the optical laser in addition to the FEL.

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Figure 5. Transient optical reflectivity changes ($\Delta R / R$) of GaAs as a function of x-ray pump–optical probe delay. The initial sub-picosecond electronic response is followed by a slower lattice response on the picosecond timescale. The initial drop can be used as an approximate measure for time zero. The solid black line represents a fit with an appropriate model function as a guide to the eyes.

In contrast to a setup in which pump and probe pulses are generated by the same laser source, the FEL and optical pulses provided at FLASH are not intrinsically synchronized. Although a master oscillator is used to synchronize the FEL and the optical laser system, the linear acceleration of the electron bunches as well as the Ti:sapphire laser produce a timing jitter which inhibits femtosecond stability of the arrival times. Thus, to increase the effective time resolution of a pump–probe experiment, one has to measure this jitter in a parasitic way on a bunch-to-bunch basis. For this purpose, FLASH provides the timing by electro-optical sampling (TEO) system, which determines the temporal delay between an optical laser pulse and an FEL pulse within each macrobunch with an accuracy of 200 fs (FWHM) [50]. More precisely, the TEO system measures the relative jitter between the optical laser pulses and the electron bunches. In addition to that, it is essential for a pump–probe experiment to have accurate information on the absolute timing between the FEL and the optical laser. The point in time when the FEL and optical pulses overlap at the position of the sample provides the absolute timing reference (time zero). It can be determined very effectively by the femtosecond x-ray/optical cross-correlator method introduced by Gahl et al [58] and described below. Once the necessary delay of the optical laser for time zero has been established the jitter between the optical laser and the FEL can be corrected during the aftermaths data processing using the TEO information correlated by means of the bunch identification number.

To determine their temporal overlap, the FEL and optical pulses are focused on a GaAs crystal located in the main experimental chamber. Reversing the scheme employed for trXPS, the FEL pulses are now used to pump the GaAs crystal, whereas the optical pump pulses probe the induced transient reflectivity changes as a function of pump–probe delay. The relative reflectivity change is measured using two identical photodiodes: one installed on the laser board behind a semipermeable mirror to measure the intensity of the incoming beam (see figure 1) and the other placed behind a window outside the vacuum chamber detecting the intensity of the beam reflected by the GaAs crystal. In order to always have an accurate unpumped reference value for the GaAs reflectivity, the optical laser is commonly run at twice the FEL repetition rate. Figure 5 shows an exemplary transient GaAs reflectivity change obtained by the described method. The onset of the reflectivity drop provides the needed criterion for time zero.
within ±0.4 ps. Note that a more accurate calibration of time zero is implicitly contained in the measured trXPS data via the laser-assisted photoelectric effect [23, 59].

The width of the reflectivity drop in figure 5 reflects the temporal jitter of the FEL macrobunches as measured by TEO and the intrinsic arrival time differences within each macrobunch [58]. Unfortunately, these effects limit the effective time resolution of trXPS measurements in the presented approach to about 700 fs (FWHM) [23, 41], which is far above the energy bandwidth limited pulse duration [49]. In the single-bunch mode of FLASH, it is, in principle, possible to achieve an effective time resolution of about 200 fs (FWHM) [50]. However, this is not a practicable option for a photoemission experiment, because it would imply a substantial reduction of the space-charge limited count rate. A more sophisticated detection scheme, which allows us to detect multiple photoelectrons in parallel at the MHz repetition rate of the macrobunch mode, would be the solution.

2.6. Summary

From the above, it should be clear that the unique characteristics of FELs, and of FLASH in particular, offer the intriguing prospect of time-resolved pump–probe PES at probing photon energies well above 100 eV but that, compared to measurements at extremely stable third-generation synchrotron radiation sources, FEL photoemission also presents a novel experimental challenge. The generally low repetition rate and the specific pulse structure demand novel detection schemes and methods of data analysis. In particular, the fluctuations inherent to the SASE process require macrobunch-resolved detection of intensities and timing during the measurements and data sorting and filtering after the measurements have been completed.

The results reported in this section demonstrate that XPS using FEL radiation is possible and practicable with an effective energy resolution of about 300 meV (FWHM) and a typical acquisition time for one core-level spectrum of about 3 min. Moreover, since spatial and temporal overlap (to within 700 fs (FWHM)) of optical laser and FEL radiation has been achieved, trXPS measurements indeed become possible. We will now show that FEL-trXPS is not only a viable but also a useful technique by measuring the sub-picosecond to nanosecond core-level dynamics in the layered CDW reference compound 1T-TaS$_2$.

3. Case study: Ta 4f core-level dynamics in 1T-TaS$_2$

3.1. The layered charge-density-wave compound 1T-TaS$_2$

With respect to the achieved experimental specifications, we have selected 1T-TaS$_2$ for our trXPS case study because this material displays interesting sub-picosecond electron dynamics associated with coexisting CDW and Mott–Hubbard physics [21, 60] as well as a distinct CDW-induced splitting of the shallow Ta 4f core levels in the range of 620–690 meV below temperatures of 180 K [57].

1T-TaS$_2$ is a layered compound made up of S–Ta–S sandwiches in which each Ta atom is octahedrally coordinated by six S atoms (1T structure). In the pristine material, simultaneously strong electron–phonon and electron–electron interactions, predominantly within the hexagonal Ta layers, produce a complex phase diagram containing several CDW phases as well as a Mott insulating phase. Moreover, upon intercalation with alkali metals or under hydrostatic...
Figure 6. (a) The hysteretic phase transition between the nearly commensurate (NC) and commensurate (C) charge-density-wave (CDW) phases in 1T-TaS$_2$, as seen in the temperature dependences of the electrical resistivity (black line [63]) and the CDW-induced Ta 4f$_{7/2}$ splitting $\Delta_{\text{CDW}}$ (blue and red symbols and blue line [57]). The $\Delta_{\text{CDW}}$ values are scaled to match our criterion for the determination of the splitting. The initial (open blue circle), intermediate (filled blue circle) and final (filled red circles) $\Delta_{\text{CDW}}$ values of our pump–probe experiments are included. Dashed black arrows indicate the excitation paths for the two excitation fluences used. (b) Schematic real space structure of the $\sqrt{13} \times \sqrt{13}$ CCDW phase showing Star of David clusters in the hexagonal Ta plane with non-equivalently charged $a$, $b$ and $c$ Ta atoms. Small black arrows indicate the displacement of the atoms from their original positions. (c) Time-averaged Ta 4f core-level spectrum measured at a photon energy of 156 eV at FLASH. Both the Ta 4f$_{5/2}$ and Ta 4f$_{7/2}$ levels are split into two peaks associated with lattice sites $b$ and $c$. The peak splitting is denoted by $\Delta_{\text{CDW}}$.

Pressure, the system enters additional CDW phases with various symmetries or even becomes superconducting [61–63]. In the present work, we will concentrate on one specific thermal phase transition in pristine 1T-TaS$_2$, namely on the hysteretic first-order transition between the low-temperature commensurate CDW (CCDW) phase, which is also Mott insulating, and the nearly commensurate CDW (NCCDW) phase around room temperature (see figure 6(a)) [64, 65].

Figure 6(b) schematically illustrates the Star of David-shaped modulation of the charge density and Ta lattice in the CCDW phase: 13-atom Ta clusters are formed consisting of two 6-atom rings (Ta atoms $b$ and $c$) which are both contracted towards the central Ta atom (atom $a$) [64] by up to 7% of the in-plane lattice constant [66]. This strong periodic-lattice distortion (PLD) is accompanied by a large-amplitude CDW, as roughly 0.4 electron is transferred from each atom $c$ in the outer ring to the inner atoms $a$ and $b$ [67]. As a result, the shallow Ta 4f core levels split into two well-separated peaks (associated with the $b$ and $c$ atoms; the $a$ peak being weak and not readily resolved [68]) (figure 6(c)). In the electronic structure, the $\sqrt{13} \times \sqrt{13}$ CDW/PLD reconstruction causes the partially filled Ta 5d-derived conduction band to regroup.
into three sub-manifolds [67, 69, 70], with the uppermost weakly dispersive and half-filled sub-band further undergoing a Mott–Hubbard-type transition as indicated by the jump in the in-plane resistivity (figure 6(a)).

The transition from the CCDW phase to the NCCDW phase is characterized by a loss of long-range phase coherence, as the NCCDW phase bears a distinct domain structure [71] consisting of (possibly insulating) CCDW domains and (possibly metallic) domain walls that may be responsible for the suppression of the Mott phase [63, 72]. The focus of our case study is on the Ta atomic-site-specific charge order dynamics across this CCDW–NCCDW transition after an impulsive optical excitation. Our ‘spectroscopic order parameter’ will be the CDW-induced Ta 4f splitting, $\Delta_{\text{CDW}}$, whose equilibrium temperature dependence is almost perfectly correlated with the resistivity curve (see figure 6(a)).

### 3.2. Time-resolved Ta 4f photoelectron spectroscopy

The trXPS measurements on $1T$-TaS$_2$ were carried out at the beamline PG2 of FLASH as described in detail above. The $1T$-TaS$_2$ samples$^9$ were held at an equilibrium temperature of 10 K, i.e. deep in the CCDW phase. FLASH was operated at a wavelength of 24 nm and the 200 lines mm$^{-1}$ grating of the monochromator selected the third harmonic of the FEL radiation at 156 eV photon energy. The optical (800 nm) pump pulses had a duration of 120 fs. Two incident fluences were used: 1.8 and 2.5 mJ cm$^{-2}$ corresponding to absorbed energy densities of 120 and 165 meV Ta$^{-1}$, respectively; in both cases enough to heat the excitation volume across the CCDW–NCCDW transition temperature ($\sim 110$ meV Ta$^{-1}$) [23]. Note that the absorbed fluences of 1.1 and 1.5 mJ cm$^{-2}$ (for a reflectivity $R = 0.39$ [73]) are significantly larger than the fluences of 0.14 [60] and 0.3 mJ cm$^{-2}$ [25] used in recent experiments to track the melting of the Mott gap via time-resolved ARPES, but comparable to the fluence of 1.5 mJ cm$^{-2}$ in a recent ultrafast electron diffraction experiment to follow the dynamics of the PLD [18]. The total energy and time resolutions, including instrumental resolutions, vacuum space-charge broadening and temporal jitter, were about 300 meV (FWHM) and 700 fs (FWHM), respectively. All measured kinetic energies were referenced to the position of the Fermi edge of the unpumped system.

Figure 7 shows a selected series of Ta 4f trXPS spectra of $1T$-TaS$_2$ extracted from the recorded data set. In the unpumped spectrum, the CDW-induced splitting of the Ta 4f$_{7/2}$–Ta 4f$_{5/2}$ spin–orbit doublet is well resolved (bottom of figure 7). Upon optical pumping, the depicted spectra reveal a conspicuous dynamics of the CDW splitting on the femtosecond to nanosecond timescale. The photo-excitation first leads to an abrupt (sub-picosecond) reduction of the splitting, which is followed by a partial recovery on the picosecond timescale (lower part of figure 7). The splitting then remains constant for several picoseconds before it relaxes to its initial value within about 1.5 ns (upper part of figure 7). Note that the spectra at longer pump–probe delays ($\Delta t \geq 100$ ps) were taken at a higher pump fluence, resulting in a decreased core-level splitting for the intermediate state.

In addition to the transient modification of the ‘spectroscopic order parameter’, all pumped Ta 4f spectra are shifted towards higher kinetic energies with respect to the unpumped spectrum. This transient shift is already present at negative delays (probe pulse arriving before the pump pulse) and relaxes with a time constant of a few hundred ps at positive delays. As will be

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$^9$ $1T$-TaS$_2$ single crystals were grown in a temperature gradient of 840–870°C in 1000 h using iodine vapor transport with excess sulphur (2.5 mg cm$^{-3}$).
Figure 7. Time-resolved Ta 4f photoemission spectra of 1T-TaS₂ for various pump–probe delays and two incident pump fluences of 1.8 and 2.5 mJ cm⁻², recorded at an equilibrium temperature of 10 K. Red dots represent the experimental data and the solid black curves are fits to the spectra using a model function described in the text. The spectra reveal a transient rigid shift towards lower binding energies, a transient reduction of the CDW-induced Ta 4f splitting and a complete recovery within 1500 ps.

shown below, this extrinsic effect can be attributed to vacuum space-charge dynamics caused by nonlinear emission of electrons due to the intense optical pump pulse.

To quantify the observed intrinsic and extrinsic effects, we have fitted the series of spectra shown in figure 7 as well as other representative spectra selected from the recorded data set with a model function (see solid black lines in figure 7) consisting of four Doniach–Šunjić lines (plus a linear background) convolved with a Gaussian. In the fits, the Gaussian width (corresponding to the effective energy resolution), the Ta 4f spin–orbit splitting and the asymmetry parameters were held constant at the known values [57].

3.2.1. Femto- to picosecond Ta 4f dynamics. The ultrafast part of the Ta 4f core-level dynamics is displayed in figure 8 at a fine temporal discretization. Within the time resolution of the experiment of 700 fs (FWHM), the CDW-induced core-level splitting ΔCDW drops from its
Figure 8. Ultrafast suppression and subsequent partial recovery of the CDW-induced Ta 4f splitting $\Delta_{\text{CDW}}$ for an incident pump fluence of 1.8 mJ cm$^{-2}$ [23]. Red dots denote the experimental data obtained by fitting the spectra in figure 7 and the solid black line is the best fit with a model function consisting of two exponentials convolved with a Gaussian representing the effective time resolution. Indicated error bars result from the lineshape fitting and represent standard deviations.

initial value of about 620 meV to about 470 meV. It then relaxes to a stable intermediate $\Delta_{\text{CDW}}$ value of about 540 meV with a time constant of $\sim$900 fs. In contrast to recent time-resolved valence-band and core-level photoemission studies of 1T-TaS$_2$ [21, 25, 60, 74], our data do not reveal oscillations of the photoemission peak positions or intensities at the frequency of the amplitude mode of the CDW. This may be explained by the fact that our experiments have been performed in the strong-excitation regime in which the amplitude mode is strongly damped due to scattering with a high density of excited electrons [19, 21, 22, 60].

We interpret the observed response as follows [23]: the impulsive optical excitation heats the electron system quasi-instantaneously to temperatures of a few thousand K and thus reduces the order in the electronic portion of the CDW/PLD. The charge order is then partially restored on the timescale of electron–phonon thermalization, as the hot electrons transfer their energy to the lattice, resulting in a quasi-equilibrium CDW/PLD state that is stationary on a timescale of several tens of picoseconds. Although in our case the quasi-equilibrium temperature reached after a few picoseconds will be higher than the equilibrium CCDW–NCCDW transition temperature, the photo-induced phase will most likely differ from the equilibrium NCCDW phase, because the formation of the characteristic (metallic) discommensuration network of the NCCDW phase should occur on a much slower timescale [75]. We believe that the photo-induced quasi-equilibrium phase will rather consist of metallic domains in an insulating CCDW background. With this qualification in mind, we have indicated in figure 6(a) the excitation and relaxation pathways within the equilibrium $\Delta_{\text{CDW}}$ versus $T$ diagram for the two pump fluences used.

3.2.2. Pico- to nanosecond Ta 4f dynamics. The long-term Ta 4f relaxation dynamics extracted from the trXPS spectra shown in figure 7 (and similar ones) is displayed in figure 9: the rigid energy shift (with respect to the unpumped spectrum) of the weaker bound Ta 4f$_{7/2}$ core level in figure 9(a) and the CDW-induced Ta 4f splitting $\Delta_{\text{CDW}}$ in figure 9(b). In the analysis, the two effects are well separable. Both time dependences can be described by a single exponential
function, but with different time constants of about 375 and 655 ps for the shift and splitting, respectively.

The fact that the energy shift relaxes nearly twice as fast as the core-level splitting lends strong support to the assumption of two independent processes. We attribute the time-dependent energy shift to pump-laser-induced vacuum space charge: the intense optical pump pulse is expected to cause nonlinear electron emission \[76\] such that the resulting low-energy photoelectrons near the sample surface will push the high-energy photoelectrons emitted by the FEL probe pulse collectively to higher kinetic energies (lower binding energies) (figure 10(a)). Since the density of the low-energy electrons near the surface decreases with increasing pump–probe delay, the energy shift relaxes towards longer delays. The time constant of the slower relaxation of the ‘spectroscopic order parameter’ \( \Delta_{\text{CDW}} \), on the other hand, is consistent with heat diffusion: via diffusion of phonons the excited and probed sample volume will cool down until the initial equilibrium sample temperature of 10 K has been reached.

We will now discuss the extrinsic space-charge dynamics and the intrinsic heat diffusion dynamics in more detail.

3.3. Pump-laser-induced vacuum space-charge dynamics

Vacuum space-charge effects are known to play a non-negligible role in all time-averaged and time-resolved PES experiments that are performed with pulsed high-brightness photon sources \[41, 53–55\] so that the experimenter commonly has to choose a compromise between data acquisition time and spectral degradation by space-charge effects (see section 2.4). In the case of time-resolved pump–probe PES experiments at high excitation densities, as in the present work, one has to consider not only the vacuum space-charge effects that are induced by
the probe pulse but particularly those that are caused by the pump pulse. Intense optical pumping generally opens new channels for the nonlinear creation of a low-energy photoelectron cloud above the sample surface: thermoemission [77] as well as pure and thermally assisted multi-photon photoemission [78]. Our experimental findings point to a thermally assisted process, as the kinetic energy distribution of the emitted photoelectrons resembles that of a recent femtosecond thermoemission experiment [77]. The electrons emitted by the pump pulse in our experiment typically have kinetic energies well below 10 eV.

These slow electrons wafting above the sample surface will affect the fast electrons ($E_{\text{kin}} \approx 120$ eV) emitted from the Ta 4f states by the FEL pulse in two different ways, depending on the sign of the pump–probe delay: for negative delays (probe pulse arrives prior to the pump pulse) the fast electrons on their way to the detector will always feel the slow electron cloud in their back, whereas for positive pump–probe delays the fast electrons have to pass through the cloud of slow electrons.

For a better quantitative understanding of these effects, we have extended our molecular dynamics model [52] to include the interaction between two distinct and delayed photoelectron clouds and simulated the pump-laser-induced space-charge dynamics for our experimental parameters. The number of nonlinearly emitted electrons was first estimated from the results of Peloi et al [78]. According to their measurements, a single optical pump pulse with a fluence of about 20 GW cm$^{-2}$, as used in our experiment, creates about 30 000 photoelectrons. However, to match the observed energy shift of 120 meV at a delay of 100 ps, we later adjusted the number of nonlinearly emitted electrons to 40 000. In the numerical simulations, the initial Ta 4f spectrum was replaced by a single 20 meV wide (FWHM) Gaussian peak centered at a kinetic energy of 120 eV. This approximation was necessary to determine the relatively weak energy broadening effects. The energy shift and broadening as measured at the detector were obtained by fitting a single Gaussian to the final kinetic energy distribution and subtracting the initial mean energy from the fitted peak position and deconvolving the initial width from the fitted peak width.
Figure 10(b) shows the simulated energy shift and broadening of the test spectrum as a function of the delay between the creation of the slow and fast electron clouds and compares the results to the ones extracted from the measured spectra. Remarkably, the simulated energy shift excellently reproduces the experimental one, its magnitude as well as its time dependence. The energy broadening, on the other hand, is much smaller than the energy shift and negligible in the experiment.

The results of the molecular dynamics simulation thus confirm our initial hypothesis that the observed relaxation of the energy shift on the timescale of a few hundreds of ps is due to pump-laser induced vacuum space charging. Moreover, the results show that this form of vacuum space charge has a negligible effect on the ‘spectroscopic order parameter’ $\Delta_{\text{CDW}}$.

### 3.4. Heat diffusion dynamics

While almost every recent time-resolved pump–probe study of complex materials has had its focus exclusively on the ultrafast timescale [21–24], we are interested here particularly in the long-term equilibration dynamics, which occurs on the picosecond to nanosecond timescale and may provide clues as to the nature of the photo-induced quasi-equilibrium state in comparison to thermal equilibrium CDW/PLD states. Specifically, we will try to connect the observed relaxation of the ‘spectroscopic order parameter’ $\Delta_{\text{CDW}}$ to the recondensation of the CCDW phase via phonon diffusion out of the optical excitation volume.

To this end, we assume that the heat dissipation process can be simulated effectively by a 1D model. At first glance, electrical transport measurements point to negligible out-of-plane heat conduction as they reveal an out-of-plane to in-plane resistivity anisotropy of $\rho_\perp/\rho_\parallel = 500$ [79]. However, the anisotropy between the spot diameter, $d_{\text{OPT}} = 1$ mm, and the penetration depth into the bulk, $z_{\text{OPT}} = 33$ nm, of the optical pump beam is two orders of magnitude larger. Thus, heat conduction parallel to the surface can be neglected and the spatiotemporal dynamics of the temperature profile in the direction perpendicular to the surface should be describable by the 1D heat equation:

$$\frac{\partial T(z, t)}{\partial t} = \frac{\lambda_\perp}{c(T)} \frac{\partial^2 T(z, t)}{\partial z^2},$$

where $\lambda_\perp$ is the out-of-plane heat conductivity and $c(T)$ the temperature-dependent specific heat coefficient.

In our numerical simulation, we have first calculated the initial temperature distribution $T(z, 0)$ using a pump fluence $F = 2.5$ mJ cm$^{-2}$, an absorption coefficient $\alpha = 3 \times 10^3$ m$^{-1}$ [73], a reflectivity $R = 0.39$ [73] and a specific heat coefficient $c(T)$ derived from the Debye model with a Debye temperature of 237 K and a parameter $\beta = 12.62$ J m$^{-3}$ K$^{-4}$ [80]. We have then solved equation (1) numerically by a finite difference method for different constant values of the heat conductivity $\lambda_\perp$.

Figures 11(a)–(c) show the resulting space and time dependence of the lattice temperature in the uppermost 200 nm of the sample for $\lambda_\perp$ values of 1, 3.9 and 11.5 W K$^{-1}$ m$^{-1}$. The first $\lambda_\perp$ value is the best fit to our experimental results, whereas the latter two values represent the measured minimum and maximum values for the in-plane heat conductivity of $1T$-TaS$_2$ at temperatures of 100 and 180 K, respectively [81, 82] (the out-of-plane heat conductivity has not been measured). Figure 11(d) shows the corresponding temporal evolutions of the lattice temperature within the first nanometer of the sample, i.e. the approximate region probed by Ta 4f photoemission at a photon energy of 156 eV [83]. To this figure, we have also added...
Figure 11. Simulated heat diffusion dynamics as obtained by numerical integration of a 1D heat diffusion equation. (a)–(c) Spatiotemporal evolution of the lattice temperature near the sample surface after an optical excitation (2.5 mJ cm\(^{-2}\)) for different heat conduction values. (d) Temporal evolution of the surface temperature for different heat conduction values. The dashed line indicates the equilibrium NCCDW–CCDW phase transition temperature. Black and gray dots indicate temperature values estimated for the experimental data shown in figures 9(b) and 6(a). Indicated error bars are the corresponding error bars of \(\Delta_1\) plus a systematic error of 10 K that is attributed to uncertainties of the equilibrium \(\Delta_1\) curve plotted in figure 6(a). Data points for surface temperatures below 180 K are indicated by open symbols to emphasize the low accuracy associated with the plateau region of the \(\Delta_1\) curve.

the experimental surface temperature as estimated from our measured \(\Delta_1\) values and the equilibrium \(\Delta_1(T)\) curve plotted in figure 6(a). Data points for surface temperatures below 180 K are indicated by open symbols to emphasize the low accuracy associated with the plateau region of the \(\Delta_1\) curve.

The time dependences of the surface temperature estimated from experiment and simulated for \(\lambda_\perp = 1\) W K\(^{-1}\) m\(^{-1}\) agree very well for delay times up to 750 ps and lattice temperatures above 200 K. But they deviate for longer times and lower temperatures, i.e. when the system has crossed the equilibrium NCCDW–CCDW transition temperature (dashed line in figure 11(d)). We expect that around this temperature the photo-induced CDW/PLD phase should transform back into the CCDW phase. Not surprisingly, the simple 1D heat diffusion model with constant \(\lambda_\perp\) does not capture this phase transition at which the heat conduction coefficient and also the dimensionality of the problem may change [81, 82]. Nevertheless, the agreement between experiment and simulation on the sub-750 ps timescale is strong evidence that the observed long-term relaxation dynamics of the ‘spectroscopic order parameter’ \(\Delta_1\) is governed by heat diffusion.
3.5. Summary

In figure 12, we schematically summarize the complete intrinsic temporal response of the CDW-induced Ta 4f core-level splitting (the ‘spectroscopic order parameter’) in $1T$-TaS$_2$ to an impulsive optical excitation. As for conventional metallic systems, the response can be divided into three phases: (i) hot electron creation and thermalization, (ii) electron–phonon thermalization and (iii) phonon diffusion, with each process happening on its own characteristic timescale [84]. For $1T$-TaS$_2$, it is particularly interesting to see how the complete sequence relates to the equilibrium phase diagram and which of the electronic (CDW) and lattice (PLD) degrees of freedom of the coupled CDW/PLD is primarily affected in each process.

Phase (i) starts with the optical excitation of a significant fraction of the valence electrons. Within less than roughly 100 fs the excited electrons thermalize into a Fermi-Dirac energy distribution with a temperature of a few thousand K. The CDW melts quasi-instantaneously, while the PLD has no time to react. In phase (ii), the excess energy in the electron system is transferred to the lattice system, thus leading to a melting of the PLD. After a typical electron–phonon thermalization time of a few picoseconds, a quasi-equilibrium CDW/PLD state has formed, in our experiments at a quasi-equilibrium temperature higher than the CCDW–NCCDW transition temperature. However, the photo-induced phase will most likely not display the intricate structure of the equilibrium NCCDW phase of $1T$-TaS$_2$ because the formation of the characteristic network of domain walls (discommensurations) is expected to happen on a much longer timescale [75]. We conceive a photo-induced CDW/PLD phase consisting of metallic islands in a CCDW background. Finally, in phase (iii), the excess heat...
within the probed excitation volume diffuses into the bulk and the system slowly condenses into its original CCDW state on the nanosecond timescale.

4. Conclusion

In the present work, we have described the realization of the technique of trXPS at the FEL FLASH and demonstrated its capability in a case study of the Ta 4f core-level dynamics in the layered CDW reference compound 1T-TaS$_2$. The most important general conclusions that can be drawn from our present results are: (i) standard (time-averaged) core-level photoemission spectroscopy using FEL radiation can be performed in an intensity regime where vacuum space-charge effects are under control. The observed FEL-induced space-charge effects are well understood, as they are fully reproduced by ab initio molecular dynamics simulations. (ii) Systematic time-resolved optical pump–FEL probe core-level PES can be performed with time and energy resolutions of at least 700 fs (FWHM) and 300 meV (FWHM), respectively, and with a typical acquisition time for one spectrum of about 3 min.

Since our experimental approach has essentially consisted of applying the conventional detection scheme that has proven successful in time-averaged high-resolution PES at third-generation synchrotron radiation sources and since, during the time the experiments were performed, the pulse repetition rate of FLASH was limited to 150 Hz, we anticipate that the capability of the technique will improve significantly in the near future. Through the use of fast and highly efficient time-of-flight photoelectron spectrometers [85] and the by now improved FEL repetition rates (of up to 8000 Hz), the acquisition time per spectrum could easily be reduced by a factor of about 50 at improved energy and time resolutions of about 50 meV (FWHM) and 200 fs (FWHM) [50], respectively. An even better time resolution is expected as soon as more sophisticated schemes for jitter determination are realized [86].

We believe that these improvements will take us a big step forward in the study of condensed matter systems far from equilibrium and at elementary timescales. The technique of trXPS with its full elemental, chemical and atomic-site selectivity will, in particular, enable us to shoot ‘electronic movies’ of charge ordering dynamics in complex materials and of chemical reactions on solid surfaces.

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