A high-order harmonic generation apparatus for time- and angle-resolved photoelectron spectroscopy

Citation: Review of Scientific Instruments 84, 075106 (2013); doi: 10.1063/1.4812992
View online: http://dx.doi.org/10.1063/1.4812992
View Table of Contents: http://scitation.aip.org/content/aip/journal/rsi/84/7?ver=pdfcov
Published by the AIP Publishing
I. MOTIVATION

Photoemission spectroscopy has proven to be a powerful tool for the investigation of electronic properties of solids. It has greatly developed, starting in the 1960s from binding energy measurements in normal emission to high resolution full k-space measurements with third generation synchrotron sources (see Ref. 1 and references therein). A big step in this development was the commercial availability of angle-resolving hemispherical analyzers. With full knowledge of the energetic band structure it was possible to examine quasiparticle interactions through their kink-like signatures in the band dispersion near the Fermi level. At the same time spin detectors were combined with energy and angular resolution to obtain knowledge of exchange-split band structures and Fermi surfaces. With this full set of measured quantities, one important piece of information left is the dynamical behavior of the solid upon perturbation, which is especially interesting for correlated materials such as ferromagnets, superconductors, charge-density-wave systems, topological insulators, or heavy fermion systems. To cover quasiparticle interactions in the time domain it is desirable to operate on the sub-picosecond timescale. In recent years this challenge has been tackled by several complementary methods including measurements with free electron laser sources, femtosecond beam slicing with conventional synchrotron sources, and the “table top” approach using a femtosecond laser-based monochromatized high-order harmonic light source, as presented in this paper. In the first step, the electric field of the laser suppresses the atomic Coulomb potential, allowing a bound electron to tunnel into the continuum. The electron is then accelerated by the laser field and returns to the vicinity of its parent ion when the field reverses. Finally, the electron recombines with the ion, releasing an extreme ultraviolet (XUV) photon with an energy that is an odd multiple of the IR photon energy. The probability of this recombination is of order $10^{-6}$ so the XUV photon yield is low and losses have to be minimized.

With the increasing availability of reliable femtosecond lasers, HHG has developed into a versatile source of XUV radiation. In addition, high-order harmonic radiation retains many desirable properties of the laser used to generate it. For use as a spectroscopic light source, the most important of these are the spatial and temporal coherences, which lead, respectively, to the formation of a collimated beam of femtosecond XUV pulses.

Most high-order harmonic generation experiments are used for their femtosecond time resolution to investigate electron dynamics in atoms and molecules in the gas phase. In contrast only a few experiments have been optimized for the investigation of dynamics in solids, and only some of those look at transient band structures. Our objective is to combine the power of angle-resolved photoelectron spectroscopy (ARPES) with the fs time resolution and XUV photon energies available through HHG, the latter allowing access to high electron momenta to probe the whole Brillouin zone. Photoelectrons generated at these photon energies have mean free paths in the material of only a few Ångström, so this technique is inherently surface sensitive and probes the first few sub-surface layers to yield information on the bulk band-structure. Since the native bandwidth of even a single harmonic generated by a 40 fs near infrared laser pulse is on the order of $0.25 - 0.5$ eV, it is desirable to select a fraction of the bandwidth. To this end we have designed and built a monochromator beamline delivering a bandwidth as small as 90 meV at 35.6 eV, while maintaining an overall time
resolution better than 150 fs and sufficient photon flux for reasonable measurement times.

Apparatuses for time-resolved photoemission studies at surfaces have been presented by several authors with distinct objectives. The main differences between the setups are the repetition rate of the laser and the photon-energy selection, which is the primary focus of this paper. Currently, there are several different approaches for wavelength selection, most common are single grating\textsuperscript{19,23,32} and double gratings\textsuperscript{29,33,34} monochromators. Generally, single grating arrangements have a higher transmission, while double grating arrangements deliver shorter pulses by compensating the tilt of the wave front incurred by diffraction from a single grating. Both approaches can be modified to make use of conical diffraction to achieve higher transmission.\textsuperscript{21,35} An alternative approach is to employ multilayer mirrors whose coating is tailored to reflect a fixed single harmonic from the frequency comb delivered in HHG,\textsuperscript{30,36,37} or to select a broad bandwidth close to the high-energy cutoff for attosecond spectroscopy.\textsuperscript{28}

**II. BEAMLINE DESIGN**

Our approach seeks a compromise between energy and time resolution, while maintaining flexibility (i.e., wavelength tuneability), a high optical throughput and reduced optical complexity. We therefore opted for a design based on a single-grating monochromator, with the grating mounted conventionally. Since the overall energy resolution of a monochromator is partially determined by the convolution of the input and output slits, it is desirable to have a mirror between the XUV source and the entrance slit of the monochromator to focus the XUV on the entrance slit. Otherwise the HHG source is effectively the entrance slit, and increasing the resolution by reducing its size (by making the IR focus smaller) may have undesirable consequences for HHG efficiency. Therefore, we included a mirror before and after the monochromator. To obtain a high reflectivity, the mirrors and grating are designed for grazing incidence and are therefore toroidal. Our design also makes use of extensive differential pumping along the length of the beamline. From $10^{-3}$ mbar at the HHG source, a pressure of better than $3 \times 10^{-11}$ mbar can be maintained indefinitely in the photoemission chamber, allowing for long measurement times without sample degradation.

To reach the desired performance, the optical design was optimized by modeling and ray tracing. The results are shown in Fig. 1. An overview of the apparatus is depicted in Fig. 2. The overall efficiency of the beamline was obtained with the REFLEC code,\textsuperscript{38} taking into account the incidence angles and the micro-roughness of the optical surfaces, as well as the specified shape of the grating profile (Fig. 1). Geometrical effects (e.g., losses at the slits) and the transmission of the IR filtering aluminium foil are not included. An efficiency of 10\% or better could be achieved over the whole energy range. Starting with a 1.5 mJ IR pulse ($h\nu = 1.5$ eV) at a pulse repetition rate of 10 kHz we obtain $10^{10}$–$10^{11}$ photons/s in a single harmonic. The spot size at the sample position has a full width half maximum (FWHM) diameter of about 130 $\mu$m.

Simulations using the RAY code\textsuperscript{39} yielded the spectral and temporal widths of the transmitted harmonic pulses as shown in Figs. 1(b) and 1(c). They where obtained by end-to-end simulations of trajectories originating from a model of the HHG source. The spectral width in Fig. 1(b) includes both the monochromator bandpass and the inherent spectral width of the respective harmonic, which was assumed to have a Lorentzian profile with a width of 250 meV (for all harmonics up to order 39), as estimated from the width of photoelectron lines obtained with our HHG setup at Helmholtz-Zentrum Berlin.\textsuperscript{40} For the 51st order, a width of 420 meV was assumed.\textsuperscript{41} These considerations demanded the inclusion of two exchangeable gratings to reach the desired energy resolution across the whole expected HHG spectrum. The low energy grating (LEG) for photon energies 15–40 eV has 200 lines/mm. The high energy grating for 35–110 eV photons has 500 lines/mm. For slit openings $\geq 100 \mu$m, the monochromator acts more or less as a harmonic filter, i.e., the complete selected harmonic is transmitted and maximum flux is achieved. Reducing the slit size yields better energy resolution, at the price of lower photon flux.

The calculated temporal pulse broadening of the harmonic by the grating is shown in Fig. 1(c). As the temporal broadening is mainly determined by the number of
FIG. 2. Layout of the IR-pump – XUV-probe tr-ARPES experiment. Approximately 90% of the Ti:S laser output is used for HHG, while the remaining 10% is used for pumping the sample. Both beam paths have their own computer-controlled compressors for pulse duration control and a $\lambda/2$ – plate + polarizer combination for power control. HHG occurs in the gas cell, typically in Ar. XUV sensitive photodiodes are located just after the Al filter and after the second toroidal mirror. The IR pump beam is introduced into the beamline after the second toroidal mirror. A BBO crystal behind the analyzer chamber is used to find the temporal overlap of the pump pulse and an IR pulse allowed to pass through the beamline.

illuminated grooves of the grating, i.e., the tilt of the wave front, it depends both on the divergence of the incoming harmonic beam and the angle of incidence on the grating. Therefore, the broadening is energy (i.e., harmonic order) dependent, but for all harmonics lies in the range of 100–150 fs according to our ray tracing.

An analytic expression for the pulse broadening may be found in Ref. 42. To first order pulse broadening stems from the lateral dispersion and is determined by the available bandwidth at each point of the exit slit, i.e., the energy resolution of the monochromator grating $\Delta \lambda = N \cdot \lambda$, where $N$ is the number of illuminated lines. For illustration we calculate the temporal broadening at 35.6 eV due to the LEG. The monochromator entrance arm is 331 mm long so, assuming a divergence of the harmonics of 4 mrad FWHM, the spot size at the grating is 1.3 mm. This is elongated to 4 mm by the grazing incidence angle of 19°. Thus 800 lines of the 200 lines/mm grating are illuminated, leading to a delay of $800 \times \lambda/c \approx 100$ fs, where the wavelength $\lambda = 34.4$ nm and $c$ is the speed of light. As the bandwidth $\Delta \lambda$ will always pass through the monochromator, the slit size sets the energy resolution but only little affects the pulse broadening (cf. Fig. 1).

The frequency shift across the beam profile (spatial chirp) of a pulse diffracted off the grating leads to group velocity dispersion (GVD). This second order pulse broadening scales with $\lambda^3 \cdot N^2$ and is moderate in our setup ($\sim$8 fs at $h\nu = 35.6$ eV).42 GVD likewise causes a frequency chirp of the pulse which we estimate to 30 meV over the 100 fs pulse duration at the sample position. The chirp leads to a small broadening of the ARPES spectra compared to the overall energy resolution of the experiment of about 200 meV. Note that this frequency shift cannot be time-resolved when probing initially occupied states.

### III. BEAMLINE REALIZATION

The layout of the beamline can be seen in Fig. 2, along with the other components forming the complete tr-ARPES experiment. Technical details of the XUV optics are presented in Table I.

The HHG process occurs in the gas cell. From there the XUV radiation co-propagates with the IR beam through two 2 mm diameter fixed apertures, which form a differential pumping stage between the gas cell chamber and the rest of the beamline. The apertures can also be used for coarse alignment and reduce the IR intensity. The rest of the IR radiation is blocked after the apertures by a 150 nm thick aluminium foil supported by a Ni mesh (Luxel Corp.) to protect the entrance slit of the monochromator and prevent the grating from heating. The measured transmission of the Al filter at 35.6 eV is about 50% and rises with higher photon energies. It is mounted on a CF40 gate valve, which aids the differential pumping of the beamline and can be opened for alignment with the IR beam or a co-propagating HeNe laser beam. As Fig. 2 shows, after the Al filter, the XUV beam is

<table>
<thead>
<tr>
<th>Optical element</th>
<th>Mirrors</th>
<th>LEG</th>
<th>HEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long radius</td>
<td>9567 mm</td>
<td>1000 mm</td>
<td>1000 mm</td>
</tr>
<tr>
<td>Short radius</td>
<td>104.5 mm</td>
<td>104.9 mm</td>
<td>104.9 mm</td>
</tr>
<tr>
<td>Deviation angle</td>
<td>168°</td>
<td>142°</td>
<td>142°</td>
</tr>
<tr>
<td>Slope error rms$^a$</td>
<td>$\leq2°/\leq5°$</td>
<td>$\leq1°/\leq5°$</td>
<td>$\leq1°/\leq5°$</td>
</tr>
<tr>
<td>Microroughness rms</td>
<td>$\leq0.5$ nm</td>
<td>$\leq0.5$ nm</td>
<td>$\leq0.5$ nm</td>
</tr>
<tr>
<td>Line density</td>
<td>…</td>
<td>200/mm</td>
<td>500/mm</td>
</tr>
</tbody>
</table>

$^a$Long axis/short axis.
focused at the entrance slit of the monochromator by a grazing-incidence toroidal mirror (Winlight). Located 1 m from the gas cell with a 500 mm focal length, the mirror relays a 1:1 image of the HHG source to the monochromator entrance slit. The monochromator grating relays an image of the entrance slit to the exit slit, and the second identical toroidal mirror images the monochromator exit slit onto the sample.

The monochromator itself is a customized Jobin-Yvon JY-VTM-EUV toroidal grating monochromator (entrance arm length 331 mm, exit arm length 320 mm) equipped with slits adjustable under vacuum for photon energy and bandwidth selection. The monochromator houses the two custom-made laminar toroidal gratings, which can be exchanged under vacuum.

Following the design of large grazing-incidence mirrors in synchrotron beamlines, we use a five-axis, six-strut arrangement with well proven reliability to support and adjust the two toroidal mirrors. The chambers housing the optical elements are on heavy granite blocks, and mechanically decoupled from the surrounding beamline by bellows. Together with the computer controlled monochromator, this ensures easy and reliable user operation of the beamline. For alignment purpose and for assessment of the harmonic photon flux, two XUV sensitive photodiodes (AXUV100, International Radiation Detectors Inc.) can be introduced into the beamline before or after the monochromator (see Fig. 2).

The vacuum chambers housing the mirrors and gratings are each pumped with a vibrationally isolated turbo-molecular pump (Pfeiffer, TMU 261P), leading to effective differential pumping along the beamline. Together with an ion-getter pump attached to the last chamber we reach ultra-high vacuum (UHV) conditions with a base pressure of $10^{-10}$ mbar in the beamline and $10^{-11}$ mbar in the analyzer chamber.

IV. THE LASER SYSTEM

In order to minimize space charge effects due to electron-electron repulsion in photoemission from solid surfaces (see discussion below), it is desirable to release approximately one electron into the spectrometer with each probe pulse. This calls for a high repetition rate laser source. On the other hand, HHG is typically and most conveniently achieved with $> 500 \mu$J pulses. This combination rapidly leads to high average power lasers. A reasonable compromise between repetition rate and pulse energy can be achieved with Titanium Sapphire (Ti:S) chirped-pulse amplifiers (CPA) running at 10 kHz and 1–2 mJ energy per pulse.

The laser chosen for our experiment is a commercial Ti:S CPA laser system (Red Dragon, Kapteyn Murnane Labs). The laser comprises a prism-compensated Ti:S oscillator running at 80 MHz followed by three helium-cooled multipass amplifier stages. Each stage is pumped at 532 nm by a 10 kHz Q-switched Nd:YAG laser (Photonics Industries, DM100-532) operating at 85 W. We have introduced a spatial filter (a 1:1 Newtonian telescope with a 200 $\mu$m diameter diamond pinhole at the focus) between the first and the second amplifier stage to avoid hot spots in the beam profile after the multipass amplifier. This incurs a power loss of $\approx 10\%$ but reliably avoids damage to the subsequent amplifier crystals. After two separate grating compressors in the pump and probe beam-paths with about 60% transmission the laser delivers 17 W at 10 kHz (1.7 mJ/pulse) with a center wavelength of 785 nm and a pulse duration of 40 fs, as measured with frequency-resolved optical gating.

Approximately 10% of the laser output is split off to excite (pump) the sample. It passes through a separate compressor, as shown in Fig. 2, allowing the pump pulse to be stretched to arbitrary durations without affecting the HHG process.

V. HIGH-ORDER HARMONIC GENERATION

Since HHG is a highly nonlinear process, it is sensitively dependent on a number of experimental parameters. In addition to the laser wavelength, the pulse energy and duration, we must also optimize the beam profile, the focusing geometry, the interaction length, and the gas pressure (and type).

To optimize focusing we tested different arrangements and found the best results using a lens with a focal length of 600 mm. The exact position of the focus is known to influence the harmonic generation efficiency through the Gouy phase, and its optimum depends on the pump pulse intensity and the gas pressure. For our experiments the best results were achieved by positioning the focus just behind the gas cell in the beam propagation direction, towards the monochromator (at 1.5 mJ, 40 fs, and 100 mbar argon). It is noteworthy that any form of astigmatism in the IR focus at this point significantly reduces the harmonic yield.

The optimum length of the cell depends on the laser intensity and therefore on the focal length of the lens, the laser pulse energy, and pulse length. We have tested a number of different types of gas cells with an interaction length between 2 and 15 mm with walls of stainless steel and copper between 20 and 200 $\mu$m thick. The best was found to be a simple stainless steel tube ($\varnothing 3 \times 0.2$ mm) with one end connected to the gas supply by compression fittings and the other flattened and folded over to seal it. The focused IR beam burns through the gas cell wall ensuring the holes have the correct diameter ($\approx 150 \mu$m) and are perfectly aligned to the beam.

The argon pressure for the gas cell is computer controlled (MKS 640) and can reach up to 200 mbar. The tuneability of this pressure is important since it has a strong influence on the spectrum of the generated harmonics. Depending on the laser intensity we have found an Ar pressure of 50–100 mbar to give the highest harmonic yield. During operation the pressure outside the cell stays below 5 $\times 10^{-3}$ mbar, corresponding to a pressure gradient of about five orders of magnitude, due to the small holes in the cell walls. The gas cell chamber is pumped by a turbo-molecular pump (Pfeiffer TMU 51P 500 l/s) backed by a piston pump (Leybold Ecdory M15).

Many parameters of the beamline that must be optimized are controlled by a lab-written software: the gas cell pressure, the grating separation of both compressors (and therefore the IR pulse lengths), the power of the pump and HHG drive pulses and monochromator grating angle, i.e., the XUV wavelength of the probe pulse. The pump and HHG drive IR pulses are characterized and optimized before each experiment using frequency-resolved optical gating. A typical XUV spectrum
using the optimized parameters described above is shown in Fig. 3.

VI. ARPES EN DSTATION

The endstation comprises three chambers separated by gate valves (see Fig. 2): A μ-metal analyzer chamber (VG Scienta), a sample preparation chamber and a sample garage.

The μ-metal chamber reduces the Earth’s magnetic field to values below 50 nT. It houses a hemispherical display-type photoelectron analyzer (Specs Phoibos 100) for ARPES. We use a peltier-cooled camera (PCO, sensicam qe) to monitor the count rates. This guarantees negligible thermal noise relative to the CCD readout noise, thus enabling measurements with exposure times of up to several minutes at each pump probe delay. To calibrate the count rate we operate the camera with a short exposure time and high readout repetition rate, which makes it possible to count single electrons. The analyzer chamber is pumped by an ion getter pump and a titanium sublimation pump, in addition to the turbomolecular pump on the preparation chamber. A further getter pump attached near the electron detector ensures low pressure throughout the analyzer. Together with the differential pumping along the beamline, these pumps allow a routine base pressure of \(10^{-11}\) mbar, thus fulfilling the special vacuum conditions required for the study of bulk and surface electronic structures of reactive samples such as lanthanide metals.

The preparation chamber is designed for sample growth and characterization. It houses a LEED device, a sputter gun, a quadrupole mass spectrometer, a coil with an iron core to magnetize samples, gas inlets, a quartz balance for monitoring the sample growth, and evaporators for molecular beam epitaxy. Attached to the preparation chamber is a differentially pumped double stage load-lock and sample garage. They facilitate quick sample exchange without breaking the vacuum in the main chambers.

A cryogenically coolable sample manipulator (Vab GmbH) carries two different samples between the preparation and analyzer chambers on a copper extension built in-house. A fixed W(110) single crystal, as a substrate for the growth of thin-film samples, such as Gd, and a holder for exchangeable samples. Both samples can be heated by electron bombardment. The tungsten crystal can be heated to 2100 K, while its temperature is monitored by a type C thermocouple inserted into a small hole drilled in the side of the crystal. The temperature of the exchangeable sample is measured with a type K thermocouple. In addition the temperature of the whole manipulator head is monitored by type E thermocouple to prevent overheating of the copper parts when heating with a built-in Thermocoax heater.

VII. ARPES: BEAML INE ENERGY RESOLUTION

We have performed a number of experiments specifically to test the performance of the beamline against its design specifications. Furthermore, we have successfully performed experiments in the field of ultrafast magnetism for which the desired performance is simply a necessity. This section describes both of these experiments and their results to give a clear picture of our tr-ARPES experiment.

As stated above, the bandwidth of a single harmonic at a central energy of 35.6 eV generated by a 30–40 fs IR pulse is typically 500 meV. Since for a monochromator grating with a given line density and beam size the convolved widths of the entrance and exit slits determine the transmitted photon bandwidth, to reduce this to 150 meV the monochromator slits must be closed to typically 20 μm.

To measure the overall energy resolution of the experiment, we turn to the well known surface state of the Cu(111) surface. Following cycles of Ar⁺ sputtering and annealing to prepare the Cu surface, we performed ARPES measurements using He I\(_\alpha\) radiation from a discharge lamp and compared the results to ARPES with the 23rd harmonic (\(hν = 35.6\) eV).

The spectra in Fig. 4 were obtained by integrating the ARPES data over 0.1 Å\(^{-1}\) range of \(k∥\). Since the linewidth of radiation from the He lamp is a few meV, the observed linewidth of the surface state is dominated by the intrinsic resolution of the electron analyzer. For the data recorded with XUV from HHG the observed linewidth is then a convolution of the monochromator energy resolution (i.e., the XUV bandwidth) and the analyzer resolution. We are therefore able to use this measurement to establish the monochromator resolution for 10 μm slit size, which was found to be approximately 90 meV at 35.6 eV photon energy.

VIII. XUV PHOTON FLUX

The XUV flux depends on many parameters of the HHG process, but for our experiments, where better energy resolution is desirable, the monochromator plays a dominant role. To achieve the resolution discussed above, we must forgo considerable flux. While this may appear to be a limitation, high fluxes lead to space-charge distortion of ARPES spectra (see discussion below). For the 23rd harmonic at 35.6 eV with the XUV photon bandwidth set to 150 meV, we typically
have a flux of $3.6 \times 10^7$ photons/s reaching the sample. This leads to approximately one electron detected per XUV probe pulse and space-charge distortion from the XUV can be neglected.

**IX. TIME-RESOLVED ARPES: TIME RESOLUTION**

For time-resolved photoemission studies, the spatial overlap of the pump and probe beams is critical. To achieve this, we image the XUV and IR spots on a phosphor-coated plate in the exchangeable sample holder with a high resolution camera. This also allows the IR and XUV spot sizes to be measured.

Temporal overlap between the IR and XUV is achieved by crossing an attenuated IR beam that has traveled along the beamline with the attenuated pump beam in a $\beta$-barium-borate (BBO) crystal (see Fig. 2). To allow the fundamental to traverse the beamline, the Al filter is removed, and the monochromator grating set to zero order. Both pump and probe beams then pass through the analyzer chamber and out of a window, and are then focused into the BBO crystal at a small angle. The pump-probe delay is then scanned until a second harmonic signal from the crossed beams is observed spatially located between them. Even though the pump and probe beam paths are 10 m long after their separation, we could not observe jitter in the pump probe delay within the time resolution of 125 fs given by the XUV pulse length.

Having found the pump-probe spatial and temporal overlap we can perform tr-ARPES to evaluate the temporal resolution. Cut to 150 meV, the bandwidth at 35.6 eV would support a transform-limited pulse duration of approximately 12 fs FWHM, assuming a Gaussian spectrum. The broadening of the XUV pulse by the monochromator was calculated to be in the order of 100 fs, as discussed above and shown in Fig. 1(c). To measure the actual XUV pulse duration, we performed a time-resolved ARPES measurement on the W(110) crystal in the geometry shown in Fig. 5(a). The crystal was pumped by a $p$-polarized 50 fs IR pulse and probed with the XUV at 32.6 eV. In the proximity of the sample surface, outgoing photoelectrons excited by the XUV can exchange energy with the electric field of the IR pulse. The exchanged energy is a multiple of the IR photon energy, leading to the formation of sidebands. The sideband amplitude as a function of time is shown in Fig. 5(b), and represents a cross-correlation function between the IR and XUV pulses from which the XUV pulse duration can be recovered. This measurement indicates that our XUV pulse duration is approximately 100 fs, giving an overall time resolution for pump-probe experiments of 125 fs FWHM.
X. TIME-RESOLVED ARPES ON GD(0001)

To demonstrate the utility of tr-ARPES with high-order harmonic radiation, we present ultrafast demagnetization data from a gadolinium thin film. If we are to meaningfully investigate the ultrafast magnetization dynamics of Gd, it is necessary to resolve the valence bands with sufficient energy and time resolution. Gd therefore presents an ideal testbed for our tr-ARPES experiment.

In addition, the nature of its magnetic ordering makes the Heisenberg ferromagnet gadolinium a model system in which to unravel equilibrium vs. non-equilibrium exchange interaction and spin dynamics. It has a half-filled 4f shell, leading to a large localized magnetic moment (7 μB) per atom. This is exchange-coupled to the (5d6s)3 valence electrons and polarizes their spins, increasing the magnetic moment by a further 0.55 μB per atom. Magnetic ordering occurs because the valence electrons are itinerant and align the moments of adjacent atoms in an indirect exchange interaction explained by the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory. Thus spin minority and majority components of the valence band are exchange-split by an energy ΔEs. It is the transient behavior of these bands that we have observed following laser excitation.

Below its Curie temperature TC of 293 K, Gd is ferromagnetic and can be driven towards the paramagnetic state by intense laser excitation. Time-resolved studies have established that the 4f spins are coupled only weakly to the lattice, giving a slow spin-lattice response-time of 40 ps. Thus laser excitation of the valence bands provides a fast spin excitation channel decoupled from slow 4f spin-lattice effects.

To prepare single-crystalline samples for ARPES, 10 nm thick Gd(0001) films were grown epitaxially on the W(110) substrate. The inset shows an ARPES image recorded for 5 min at the analyzer hemispheres together with the analyzer entrance slit width of 0.5mm, this image took 5 min to record (10 repetitions of 30 s). These settings reduce the energy resolution significantly compared to the ultimate values discussed above. It could be improved at the cost of count rate by choosing a smaller entrance slit of the analyzer, changing the lens mode for a smaller acceptance angle and reducing the pass energy. If these settings are needed for comparing spectral features spread over a wide range of energies and points in k-space, as in our case the Gd 4f state at about 8 eV binding energy and the surface state at the Fermi edge together with the dispersion of the valence band, then the limiting factor is the size of the analyzer hemispheres together with the analyzer entrance slit width.

A photoelectron spectrum is extracted from the ARPES image by integrating over a small range of k0 around the Γ point, as indicated by the highlighted strip in the figure. The resulting spectrum is then fitted by 5 Lorentzians representing the surface state, the 4f level (bulk and surface component) and the majority (blue) and minority (red) spin components of the valence band. A linear background accounts for elastic electron scattering from degenerate points in the Brillouin zone and the bulk states contribute to a Shirley background. The Shirley background is assumed to be proportional to the area of the peak above the background to lower binding energies. Best fit results were obtained by convolving the spectra with a 210 meV instrument function to model the energy even distribution.

FIG. 6. Photoemission spectrum from a 10 nm thick Gd(0001) film on a W(110) substrate. The inset shows an ARPES image recorded for 5 min at one pump-probe delay using the 23rd harmonic at 35.6 eV. A photoelectron spectrum (blue points) is extracted by integrating over the highlighted stripe around k0 = 0. This is then repeated for all pump-probe delays. The energy bandwidth of the XUV was 150 meV. The electron analyzer, set to wide angle mode (±13° acceptance angle) at a pass energy of 60 eV and an entrance-slit width of 0.5 mm, has a calculated energy resolution of 150 meV FWHM. The upper limit of the total energy resolution is given by the 260 meV FWHM of the Gd surface state. The individual components used to fit the data (solid lines) are explained in the text.
XI. SPACE-CHARGE EFFECTS IN tr-ARPES

Space-charge distortion of ARPES spectra occurs when a cloud of low-energy electrons is formed at the sample surface, either through secondary electron generation by high energy electrons excited by an XUV photon, or by electrons lifted just above the vacuum level by a lower energy photon. Outgoing photoelectrons experience acceleration by the electric field of this cloud that is dependent on their emission time and energy. This leads to energetic shifting and broadening of the photoemission spectral features and is thus a severe restriction for measurements with already moderate resolution. Space-charge is known to be a problem in time-resolved photoemission studies from solid surfaces, especially for experiments with high pulse energies (typically at low repetition rates).46,54,55

We observe space-charge effects in our experiment from both the IR and XUV excitations, and both can significantly distort the spectra. Fig. 9(a) shows the effects of space-charge generated by photoelectrons excited by the XUV pulse. The data are extracted from changes in the width and energetic position of the surface state (Fig. 6) as a function of the XUV flux. XUV space-charge effects become observable when the flux from the monochromator is higher than $\approx 10^4$ photons/pulse ($h\nu = 35.6$ eV), so at the XUV fluences we measure with, the space-charge effects can be neglected. As Fig. 9 confirms, XUV space-charge distortions are approximately linear over a wide fluence range.54 At a flux of about $10^5$ photons/pulse, the XUV induced space charge shifts the spectrum by 200 meV, and is accompanied by a decline of the energy resolution by an additional 300 meV FWHM. Broadening of the spectra by XUV space-charge comprises two effects: acceleration of the outgoing electron and pulse-to-pulse fluctuations in the HHG process. The latter broadens the spectrum further due to integration over spectra that have experienced different energy shifts. It is for this reason that the broadening in Fig. 9(a) is larger than the energetic shift, in contrast to the equivalent results for IR-induced space-charge distortions, which are discussed next.

Space-charge distortion from electrons excited by the IR pump pulse is more complicated because it is delay-dependent. In dynamical spectra its compensation requires a spectral feature that does by its nature not move. In our Gd(0001) measurements the 4f level, with a binding energy resolution. The width of the Gd surface state of 260 meV (FWHM) sets an upper limit to the overall energy resolution of the photoemission experiment. The minority (blue) and majority (red) spin components of the exchange split valence band are found initially at 1.39 and 2.25 eV binding energy, respectively. These values are in excellent agreement with synchrotron measurements.53 The exchange splitting $\Delta E_{x}$, is the difference in binding energy of the two valence band components. Of particular interest is the collapse of this exchange splitting, because, at least under thermal equilibrium conditions, it can be used as a direct measure of the sample magnetization. Therefore, spectra are decomposed as described above for every pump-probe delay. Evidently, our experiment has sufficient energy resolution that these peaks can be distinguished from each other by the fitting routine. Fig. 7 shows that indeed this was possible, allowing us to independently monitor the binding energies of the two bands for all pump-probe delays. Crucially, these data show different dynamical behavior in the minority and majority bands, which had not been observed previously or predicted theoretically.51

The data above were recorded with the IR pump pulse stretched to $\approx 300$ fs to reduce space-charge distortion (see below) without losing temporal resolution of the key changes in the spectra. When the IR pulse was compressed to $\approx 50$ fs and the sample warmed to 210 K, we observe that the minority band reacts within the experimental time resolution. This measurement, shown in Fig. 8, offers another measurement of the cross-correlation between the XUV and the IR, confirming the value shown in Fig. 5.
of 8 eV, cannot be excited by the IR pump pulse. Furthermore, we measured the binding energy of this level as a function of temperature using He I radiation and found it to show no significant shift (<5 meV in the temperature range of 100–300 K). Thus, we can use any observed temporal shift of the 4f level to correct for the IR-induced space-charge distortion. Its extent is summarized in Fig. 9(b) as a function of absorbedfluence. At low fluences we see a linear increase in the peak shift and a small linewidth broadening with a sudden rapid increase at about 1.5 mJ/cm². To excite an electron from the Fermi energy to the vacuum level requires, for Gd with a preparation-dependent work function of 3.0–3.7 eV, at least two 1.5-eV photons, so this curve can be interpreted as a nonlinear increase in multi-photon absorption.

With knowledge of the IR-induced distortion, we correct all time-dependent spectral shifts to those of the 4f level to eliminate energetic shifts. We can therefore be certain that space-charge effects are not responsible for the dynamics observed in Fig. 7. However, since two-photon absorption scales with the intensity, these findings put an upper limit on the IR intensity we can employ to demagnetize the sample if we are to retain sufficient energy resolution. Thus, a balance must also be struck between time resolution and pump pulse energy (fluence): a shorter pulse with less energy or a longer one with more.

XII. CONCLUSION

We have described the design, construction, and operation of a novel monochromated tr-ARPES experiment. Its experimental realization matches the calculated performance well. The experiment exploits the femtosecond time resolution of XUV pulses from high-order harmonic sources without sacrificing the energy resolution necessary to capture interesting details of the band structure. This makes high-order harmonic radiation a powerful source for the investigation of band dynamics in solids. Tr-ARPES studies based on HHG will give new insights into the physics of correlated electron materials. XUV space-charge effects will make it favorable to design HHG sources with a repetition rate even higher than 10 kHz. Elevated repetition rates will make it possible to combine spin-, time- and angle-resolved photoemission in future experiments.

ACKNOWLEDGMENTS

We gratefully acknowledge funding by the Deutsche Forschungsgemeinschaft through Grant No. WE2037/4-1, by the Leibniz graduate school Dynamics in New Light and by the Helmholtz Virtual Institute Dynamic Pathways in Multidimensional Landscapes.
