Two-color synchrotron X-ray spectroscopy based on transverse resonance island buckets

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We report on a novel multi-color method of X-ray spectroscopy at a Synchrotron radiation source that uses two simultaneously filled electron orbits in an electron storage ring to generate multiple soft or tender X-ray beams of different wavelength. To establish the second orbit, we use nonlinear beam dynamics in the so called TRIBs—transverse resonance island buckets—mode of the BESSY II storage ring, where a second electron orbit winds around the regular one leading to transversely separated source points. X-ray beams of multiple colors are generated by imaging the individual source points via different pathways through a monochromator. The particular colors can be varied by changing the traversal electron beam positions through storage-ring parameters and/or via the monochromator dispersion. As a proof of principle, X-ray absorption spectroscopy is performed on thin Fe films in transmission as well as a scanning transmission measurement on a Fe₃GeTe₂ sample of inhomogeneous thickness normalizing resonant signals with the pre-edge intensity. Using the extraordinary pointing fidelity of successive X-ray macro-pulses arriving at MHz repetition rates, a detection of tiny contrasts in diluted systems, contrast enhancement in X-ray microscopy as well as fast dynamics studies come into reach.

Resonant X-ray spectroscopy and microscopy are indispensable tools in modern materials science for quantum and energy materials, in life- and environmental sciences as well as metrology and they will be boosted in near future by the new modern 4th generation light sources¹ coming to life. To deal with contributions to X-ray spectra that are not sample related like energy dependence of the photon flux or the detection efficiency and in particular fluctuations in the x-ray beam intensity and pointing, usually a reference value of the photon flux is recorded, ideally this is done as close to the sample as possible, i.e. without additional modification by further optical components and with a well calibrated detector. Moreover, since fluctuations in x-ray beams occur over a wide range of frequencies, the reference signal should best be measured simultaneously of quasi-simultaneously and on the shortest possible timescale. Common methods for soft x-ray experiments are (i) DC measurements of photocurrents from upstream mirrors, or (ii) upstream gold-meshes or (iii) a part of the beam (e.g. other diffraction order) is reflected to a separate detector providing a reference signal. Usually, a reference signal of the same photon energy is being used, but for some experiments a reference signal of different x-ray energy is preferable. In the present paper we show how to use an electron storage ring mode in which the electrons circulate in an orbit that closes only after three revolutions together with a direct imaging monochromator to provide time-separated X-ray signals on one single detector that alternate with MHz frequency between three different x-ray energies separated by several eV. Apart from the energy offset the different x-ray signals are fully equivalent and can serve as reference signals for each other. We demonstrate this here in a proof-of-principle experiment using the near-edge absorption of a thin film of the dichalcogenide Fe₃GeTe₂ at the Fe L₃,₂ edges by measuring transmission spectra with monochromatic macropulses emitted from electrons of successive turns in the TRIBs mode²–⁵ at single island population³ (SIP) at BESSY II.

We demonstrate how to use this for solving a contrast problem in scanning X-ray transmission spectroscopy from a challenging sample with variable thickness: With an off-resonance reference signal we can determine the local sample thickness quasi simultaneously and independently from the spectroscopic information. As the non-resonant reference beam is produced by the same electrons as the resonant beam, it contains the information of fluctuations in the storage ring down to sub-µs time scales and can be used to normalize these out. Such MHz normalization can improve the signal-to-noise ratio by orders of magnitude because the pointing stability

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of electron- and photon beams on micro-second time scales is up to 5 orders of magnitude better than for comparing signal and reference in the second or minute regime—the beam “stands still” between successive turns but jitters much more in the low frequency band owing to vibrations and other sources6. Furthermore, the non-resonant reference beam co-propagates with the resonance beam allowing for high flexibility in the experimental design. Both beams can generally be detected with the same detector separating the resonant and non-resonant signal via their arrival time on the detector. All this enables high contrast and unprecedented sensitivity for dilute species and for samples where a reference signal \( I_0 \) is hard to get.

Our approach is to convert a transversal offset in the electron beam position into an energy shift. We start by estimating the size of the effect. In the soft and tender X-ray region, grazing incidence grating monochromators7 act as workhorses that image the source point in the storage ring along the dispersion plane onto an exit slit. We used the planar grating monochromator (PGM), here at the PM3 beamline at BESSY II8. We begin by estimating how much the photon energy, \( E \), on the sample behind the slit shifts when the source point is set transversally off in the dispersion plane.

The angular dispersion relation \( \frac{dE}{dy} \) for a vertical source displacement \( dy \) (see Fig. 1) for a collimating PGM monochromator is derived (see Supplementary Note 1) according to Petersen8 and Follath’s9 work for grazing angles \( \alpha \) on the grating:

\[
\frac{dE}{dy} = \frac{2 \sin \alpha}{GhcF}
\]

where \( hc \) is the product of Planck’s constant \( h \) and the speed of light \( c \), \( F \) is the focal length of the pre-mirror and \( G \) the groove density of the blazed grating (here \( G = 1221 \) l/mm). PGMs at BESSY II are operated with light collimated along the dispersion plane by a toroidal pre-mirror under fix focus conditions8,9 at the ratio \( \cos \gamma = \frac{c^2}{c^2_{\text{ff}}} \). For the grazing incidence angle \( \alpha \) on the grating vs. photon energy \( E \) follows:

\[
\alpha(E, c_{\text{ff}}, G) = \cos^{-1} \left( \frac{hcG}{E(1-c_{\text{ff}}^2)} \right) + \sqrt{1 + \left( \frac{c_{\text{ff}} hcG}{c_{\text{ff}}^2 - 1} E \right)^2}. \tag{2}
\]

Figure 1. Sketches of the dispersion performed by a collimating plane grating monochromator and source point images from a dipole (a, b) which lay flat at a decoupled machine (c) and are displaced in the \( y \)-plane (d) forced by different skew-quadrupole settings. Charge displacement by \( \Delta y \) along the dispersion plane in (b) translates into a spectral separation \( \Delta E \) behind the exit slit of direct imaging monochromators (e.g. a plane grating monochromator) leading to a change in color of light that hits the sample (here in transmission geometry). Here, \( \gamma, \alpha \) denote grazing incidence angles on the pre-mirror \( M_s \) and the grating, respectively. Light of the same energy from a displaced bunch is blocked by the exit slit but rays of different energy from the two sources may only pass if they follow the same angle \( \beta_1 = \beta_2 \), the grazing angle of the rays reflected by the grating.

We note in Eq. (1) with (2) that the dispersion depends on the \( c_{\text{ff}} \) value and the groove density of the grating, both useful to tune the desired energy shift \( \Delta E \) at a fixed accelerator setting by a few eV while preserving resolution and flux. For \( E = 700 \) eV and \( c_{\text{ff}} = 2.25 \) (standard value) Eq. (1) yields \( \frac{dE}{dy} = 0.81 \) eV/mm (\( \sin \alpha = 0.032 \), \( \alpha = 1.84^\circ \)). Given that using TRIBs population can displace the electron beam by up to 10 mm (see Methods section), this would enable tunable energy shifts of up to 10 eV. Using another grating with \( G = 600 \) l/mm would
Results and discussion

To detect a spectral shift expected from Eq. (1), we filled 300 out of 400 possible bunches of the regular orbit leading to a pulse train of 600 ns separated by 200 ns dark gap. The signal transmitted through the sample was measured simultaneously for three successive revolutions of the electron beam in the island orbit producing a temporal pattern like the gray line in Fig. 2a: The electron beam takes three round trips before its orbit is closed. Every round trip the same bunch produces an X-ray signal of equal intensity. The temporal structure of the X-ray macro pulses corresponds to the filling pattern of electron bunches in the storage ring. When we place an iron transmission sample in the beam and tune the monochromator to 709 eV photon energy, i.e., to the transmission minimum on the “white line” of the Fe L₃ resonance, a temporal pattern as denoted by the colored curves in Fig. 2a is obtained. We now see the signal from the overall fill pattern with different intensity for the individual round trips. The reason for the different intensities becomes clear when we scan the monochromator to record the full transmission spectrum across the L₁ and L₂ edges in Fig. 2b. As expected, we see three different iron absorption spectra for x-rays emitted during different round trips. For the nominal monochromator setting of 709 eV used for the trace in Fig. 2a, the transmitted intensity of the signal from the 1st turn is weak, because the x-rays from this turn have a photon energy close to the resonant absorption maximum. X-rays from the 2nd turn are blue shifted as one needs a higher nominal monochromator energy to reach the absorption maximum; in the scan of Fig. 2a their photon energy was below the absorption threshold so that less signal is absorbed and higher intensities are transmitted through the sample. On the third turn, the photon energy is again near the absorption maximum.

The traces from the different turns are in fact identical in intensity and shape, except for their different photon energy; this shows Fig. 2c. It was generated by shifting the 2nd turn by ΔE = 2.72 eV and the 3rd turn by ΔE = 0.42 eV. The spectra shifted such are essentially identical in intensity and energy resolution, which makes the signals from different turns well suited to reference one against the other. A corresponding close-up of the L₃ region for different (coupled) accelerator settings is also depicted in Supplementary Fig. S4 compared to a near zero vertical displacement in a decoupled machine as reference.

We will now make use of this multi-color beam to map out the resonant and off-resonant transmission through a sample of spatially varying thickness quasi simultaneously: As sample for this application we use a thin flake from the dichalcogenide Fe₃GeTe₂ exfoliated from a bulk sample and mounted on a Cu-mesh (Fig. 3a, for details see Supplementary Fig. S5). As can be seen from the photograph with the sample backlit (upper right), because of the exfoliation process, the sample itself has different thicknesses. A resonant transmission experiment aiming at x-ray spectroscopy from this sample, the transmission at a given sample spot and x-ray energy depends on the electronic properties in that spot as reflected in the x-ray absorption spectrum but also on the sample thickness. Spectral changes mostly affect the energy region of the resonant absorption lines while thickness changes affect the whole spectrum. With two x-ray energies we are now able to separate the two contributions. We use one x-ray signal from the pre-absorption-edge region to determine the thickness variations across the sample and a second x-ray signal at the L₃ absorption line to do spectroscopy.

To this end, we scanned sample across the x-ray beams and sorted the signals from the different x-ray colors by their arrival times on the detector (Fig. 2a). In this way we obtained three spatial maps, out of which we used those two with maximum energy difference. For a monochromator energy of 709 eV one signal is recorded near the absorption maximum and the other at the pre-edge (dashed line in Fig. 3c). A sample map showing only the resonant absorption distribution obtained in this way is presented in Fig. 3b. The procedure is described in the Supplementary Note 2 and Supplementary Fig. S6-10: we correct for the horizontal offset and then use the pre-edge signal to determine the thickness contribution and normalize that out of the spectroscopic signal at the absorption maximum.
We expect this particular sample to be homogeneous, so the spectroscopic changes should vanish when properly normalized. Figure 3d shows a vertical line cut at the position marked in Fig. 3b: The red curve is the raw signal at the photon energy of the absorption maximum. Plotted is the absorption, which shows a huge peak at around \( z = 0.75 \) mm and other pronounced maxima at the sample edges near \( z = 0 \) mm and \( z = 1.8 \) mm. When using the pre-edge signal to normalize out thickness variations the scan becomes considerably more flat (green curve in Fig. 3d) showing the overall success of the approach.

The normalization is probably not perfect and leaves, e.g., some residual of the strong peak in the raw signal around \( z = 0.75 \) mm behind. We assign this for the way we corrected to the horizontal offset, particularly since the offset was not commensurate with the horizontal step size, which required interpolation. Still, this example illustrates the potential of the technique especially for a horizontally dispersing monochromator that ensures that all colors hit the same sample spot quasi simultaneously.

**Conclusions**

We have shown in our proof-of-principle experiment using near-edge spectroscopy in the X-ray range that the combination of transverse offset of the source points in an electron storage ring and direct imaging monochromators (e.g. PGMs) allow tunable energy shifts of a few eV at \( \approx 700 \) eV. Since the transverse position of the source point at a beamline always changes turn-by-turn when the storage ring is operated in TRIBs mode, the sample behind the exit slit is illuminated with a different color every turn (800 ns at BESSY II) at very high transverse pointing fidelity. Different source spots defined by the special static TRIBs orbit closing after three revolutions enable one to normalize resonant absorption signals on the MHz scale to, e.g., the pre-edge intensity, by simultaneous signal acquisition of successive turns and thus to directly measure true resonant absorption signals in imaging methods for chemical mapping. Since our monochromator at a 3rd generation Synchrotron Radiation source has vertical dispersion planes to adapt to the flat elliptical source, we shifted the source points vertically.
for our proof-of-principle experiment. With the help of a monochromator with horizontal dispersion plane and at a "round" source point expected from new 4th generation facilities, however, arrangements for such TRIBs applications will promise new opportunities (beyond fast polarization switching\textsuperscript{12}) for spectro-microscopic techniques with unprecedented elemental contrast and sensitivity as well as much faster data acquisition.

Methods

Accelerator and TRIBS. The two-color experiment is based on a turn-by-turn displacement of source spots at the position of a beamline. Therefore, the TRIBs\textsuperscript{2} setting at BESSY II\textsuperscript{3–5} has been used, which generates a special static island orbit in the storage ring, which is winding around the reference/main orbit in the horizontal plane, closing after three revolutions. Depending on the storage ring setting, both orbits (island and main) can exist in parallel and store different electron beams (see inset (d) in Fig. 1), but also only the island orbit alone can be populated with electrons, as it was used for this experiment. The displacement of the source spots depends on the horizontal working point (tune) of the storage ring and its distance towards the 3rd order resonance as well as the tune-shift-with-amplitude are defined by non-linear sextupole magnets. The standard orbit closing after one revolution can store up to 400 electron bunches at BESSY II. The island orbit, due to the three folded

Figure 3. Images, spectra and analysis from a dichalcogenide Fe\textsubscript{3}GeTe\textsubscript{2} thin film sample. (a) Visible light microscope image of the free standing thin film in reflection and a close up in transmission in the inset. (b) A transmission X-ray image as normalized turn by turn (turn #3/turn#1) at 709 eV. (c) Corresponding absorption spectra integrated over the full field across the Fe L-edges. (d) Raw intensity signal behind the sample at 709 eV along the vertical white line of the full map in (b) without (red) and after (green) turn-by-turn normalization (#1/#3) that eliminates the thickness contrast according to Lambert–Beer’s law, which fully dominates the raw signal (red). For detailed analysis of the maps and the line scan see Supplementary Note 2.
As a usual monochromator setting we used the G = 1221 l/mm grating at cff = 2.25 (we tested also cff = 1.4…12), from vertically separated source points in the storage ring hit the sample behind the slit at different energies. The experiments were performed in the scattering chamber behind PM3 monochromator placed on bending magnet DIP112 at section H11 at the BESSY II storage ring. The monochromator is a collimating plane grating monochromator (PGM), a successor of the famous SX700 type, that images the source point vertically de-magnified onto the exit slit and horizontally 1:1 onto the sample (see optical layout in Supplementary Fig. S2) which is part of our conceptual approach, namely that photons images the source point vertically de-magnified onto the exit slit and horizontally 1:1 onto the sample (see Figure 1). Displacements of up to 10 mm at all available source points, including the straight sections along the electron closed orbit are possible this way.

During the past few years we have provided special dedicated user weeks of BESSY III in TRIBs mode to figure out if a potential second orbit wit single bunch population in regular ToUp mode is feasible. The result was that is indeed possible to tweak most of the beamlines in a way to either accept the second or the regular orbit. If only a part of the fill pattern (e.g. the camshaft bunches for time-resolved studies) are kicked to the TRIBs orbit, these bunches can be inhibited by gate pulses if fast detectors are used. However, there are users with slow detectors being only interested in CW operation at highest performance without gating capabilities who might feel disturbed. Hence, we are aiming at dedicated user weeks in TRIBs mode e.g. with all bunches in TRIBs orbit, in the same manner we are operating the so-called low-a operation (2 weeks/year) or single bunch mode (4 weeks/year) for users with interest in special beam properties. If the TRIBs approach will turn out to be beneficial for most users, even a standard operation can be envisaged, especially at our 4th generation successor BESSY III, where the separation of point like sources in all beamlines will be easier and can be planned from the beginning.

Monochromator and experiment. The experiments were performed in the scattering chamber behind the PM3 monochromator located on bending magnet DIP112 at section H11 at the BESSY II storage ring. The monochromator is a collimating plane grating monochromator (PGM), a successor of the famous SX700 type, that images the source point vertically de-magnified onto the exit slit and horizontally 1:1 onto the sample (see optical layout in Supplementary Fig. S2) which is part of our conceptual approach, namely that photons from vertically separated source points in the storage ring hit the sample behind the slit at different energies. As a usual monochromator setting we used the G = 1221 l/mm grating at cff = 2.25 (we tested also cff = 1.4…12), 100 μm exit slit and circular polarization (S = $+ 0.4$). The grating can be easily changed to 600 l/mm at the PM3 using stepping motor controls. At other similar monochromators up to 3 gratings from 150 to 2400 l/mm are routinely available to change the line density within few seconds.

As detector we employed a windowless Avalanche Photodiode (APD) of 3 mm active area from Hamamatsu S8664-30 K (140 MHz bandwidth). The trigger was the 1/3 sub-harmonic (416 kHz) of the 1.25 MHz revolution trigger derived by a freely programmable gate array (FPGA) based divider (BMESG08-p) from the optically distributed 500 MHz master-clock signal as gated by the 1.25 MHz bunch clock trigger. Signal acquisition was performed by (i) a LeCroy 4 Gs/s oscilloscope and (ii) a Zürich Instruments UHFLI lock-in amplifier with a two-fold digital boxcar feature, respectively. For the two-color imaging applications at excellent signal-to-noise using 4 gate windows for signal and baseline acquisitions, the macro-pulse signal from the full fill pattern consisting of 300 bunches at 200 ns dark gap, the latter used as reference signal for baseline detection. The UHFLI (ii) boxcar turned out as a good pick for the spectral results in Fig. 2 we used a transmission sample of 15 nm Fe on Si$_3$N$_4$, which shows a 50% absorption dip at the Fe L$_3$ edge. The sample for the scanning imaging example from Fig. 3 was a thin freestanding film of the dichalcogenide magnetic 2D material Fe$_3$GeTe$_2$ (see Supplementary Fig. S5) of variable thickness on a copper mesh leading to an average resonant absorption of likewise ca. 50% at the Fe L$_3$ edge. The material, a van der Waals magnet, is of relevance for potential voltage-controlled magneto-electronics but used here as...
a challenging case to demonstrate our new two-color method that allows for separating thickness contrast from resonant absorption and a potentially much higher contrast by MHz normalization in microscopy applications.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: 20 June 2022; Accepted: 24 August 2022
Published online: 01 September 2022

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Acknowledgements
Financial support at BESSY II was given by the German Bundesministerium für Bildung und Forschung (BMBF). We thank D. Ponwitz for technical support at the beamline and with the detector setup. KH thanks C. Schroder for software support at the timing hardware. We are indebted to G. Schwietz and the entire machine diagnostics group for enabling the use of the streak camera.

Author contributions
K.H., C.S.L., P.G., and N.P. conceived the research. P.G., M.R., K.H., C.S.L., T.K., D.Z., Y.W.W., M.K. and N.P. contributed from all authors.

Funding
Open Access funding enabled and organized by Projekt DEAL.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-022-19100-z.

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