



Multidimensional and Multimodal Soft X-ray Methods for Quantum Materials Research

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Abstract

Quantum materials are governed by a complex interplay of spin, orbit, charge and lattice degrees of freedom, resulting in emergent phenomena like high-temperature superconductivity, charge and orbital ordering and insulator-to-metal transitions (IMTs). Often, the interaction of these subsystems results in an energy landscape with multiple local minima favouring different phases. In many cases, two or more distinct phases coexist and the macroscopic property of the material is shaped by the properties of the individual phases as well as their interaction. To understand the complexity that shapes quantum materials, their properties need to be studied in multiple dimensions of space, energy and time.

X-rays are indispensable tools for the study of quantum materials as they enable probing on atomic length scales as well as excitation of electrons bound in specific core levels. Synchrotron radiation sources provide the coherence, spectral brightness, flexible focusing capabilities and tunability of the photon energy to adapt the Xray beam properties to the requirements of a specific measurement scheme and sample. The photon energy can be tuned to electronic resonances of one element to disentangle its role for macroscopic functionality. Free-electron lasers (FELs) extend this capability in the time domain down to pico- and femtoseconds, the time scales of atomic and electronic motion.

This thesis presents the development of multidimensional and multimodal soft X-ray methods that can be tailored to address specific scientific challenges posed by quantum materials. Multidimensional studies of incident and emitted photon energies and spatial and temporal dependencies as well as the dependence on fluence of a pump laser that drives e.g. an IMT are discussed. Multimodal studies allow observing quantum materials from the point of view of different experimental techniques, like X-ray imaging, X-ray absorption spectroscopy, X-ray emission spectroscopy, (resonant) X-ray diffraction, resonant inelastic X-ray scattering (RIXS) and angle-resolved photoemission spectroscopy (ARPES).

First, the RIXS imaging method, which utilizes a transmission Fresnel zone plate to combine soft X-ray absorption spectroscopy with microscopy with a resolution of 1.8 µm, is presented. This method is applied in a study of the IMT of vanadium dioxide (VO₂) microsquares measuring $30 \,\mu\text{m} \times 30 \,\mu\text{m}$. Imaging X-ray absorption spectroscopy (XAS) shows that the phase transition temperature at the edges of the squares is lower in comparison to the centres by 1.2 K. This implies that bulk properties of quantum materials may change upon structuring on the microscale.

Second, this method is transferred to imaging X-ray diffraction (XRD) to investigate the doped titanate $Y_{1-x}Ca_xTiO_3$ with x = 0.37, revealing insulating and metallic phases which coexist in curved, striped domains across unusually large temperature regions. This observation is related to a varying chemical inhomogeneity

of about $x \pm 0.01$, likely arising during crystal growth.

Next, excitation of the electronic subsystem in quantum materials with femtosecond infrared laser pulses also drives insulator-to-metal transitions. For the study of ultrafast dynamics of magnetite (Fe_3O_4) at an FEL, zone plates can also be used for time-to-space mapping, recording a delay range of several picoseconds as well as an extended fluence range simultaneously. This time-to-space mapping setup combines temporal, spatial and pump fluence information and may be developed to record single-shot experiments in the future.

Lastly, a method, termed photoelectron spectrometry for the analysis of X-rays (PAX), which converts RIXS photons to photoelectrons via the photoelectric effect, is developed towards high energy resolution to investigate a sample from the family of high-temperature superconducting cuprates. PAX enables simultaneous recording of a range of photon-sample momentum transfer, corresponding to a significant part of the first Brillouin zone in the investigated system. In comparison to grating-based RIXS spectrometers, a PAX instrument is much more compact, saving money and experimental space. The success of the PAX method resulted in the development of a dedicated ultra-high vacuum chamber, soon to be commissioned, which promises a significant improvement in photon count rate and energy resolution, as well as the combination with ARPES.

In summary, this thesis presents experimental developments that enable the study of quantum materials through the utilisation of diverse soft X-ray methods in conjunction with a spatial resolution on the micrometer level, temporal resolution on the level of 100 fs and energy resolution on the level of 100 meV. Furthermore, it outlines concepts to improve this energy and spatial resolution by approximately one order of magnitude. The advancement of the experimental tools described in this thesis will facilitate a deeper comprehension of the complexity of quantum materials and enable us as a society to harness phenomena occurring in quantum materials.

Kurzfassung

Quantenmaterialien werden durch ein komplexes Zusammenspiel von Spin, Orbit, Ladung und Kristallgitter charakterisiert, was emergente Phänomene wie Hochtemperatursupraleitung, Ladungs- und Orbitalordnung und Isolator-Metall-Übergänge hervorrufen kann. Häufig erzeugt die Wechselwirkung dieser Freiheitsgrade eine Energielandschaft mit mehreren lokalen Minima, welche verschiedene Phasen begünstigen. Dies kann dazu führen, dass zwei oder mehr unterschiedliche Phasen koexistieren und die makroskopische Eigenschaft des Materials durch die Eigenschaften der einzelnen Phasen sowie deren Wechselwirkung bestimmt wird. Um diese Komplexität, welche Quantenmaterialien charakterisiert, zu verstehen, müssen ihre Eigenschaften in den Dimensionen von Raum, Energie und Zeit untersucht werden.

Röntgenstrahlen sind unverzichtbare Werkzeuge für die Untersuchung von Quantenmaterialien, da sie die Untersuchung auf atomaren Längenskalen sowie die Anregung von Elektronen, gebunden in spezifischen Kernniveaus, ermöglichen. Synchrotronstrahlungsquellen bieten die Kohärenz, spektrale Helligkeit, flexible Fokussierungsmöglichkeiten und Durchstimmbarkeit der Photonenenergie, welche nötig sind um die Eigenschaften des Röntgenstrahls an die Anforderungen eines bestimmten Messschemas und einer bestimmten Probe anzupassen. Die Photonenenergie kann auf elektronische Resonanzen eines Elements eingestellt werden, um dessen Beitrag zu der makroskopischen Funktionalität zu untersuchen. Freie-Elektronen-Laser (FELs) erweitern diese Möglichkeiten hin zu den Zeitskalen von Piko- und Femtosekunden, auf welchen sich Atome und Elektronen bewegen.

Diese Dissertation beschreibt die Entwicklung von multidimensionalen und multimodalen Weichröntgenmethoden, welche auf die spezifischen wissenschaftlichen Herausforderungen von Quantenmaterialien angepasst werden. Multidimensionale Studien von einfallender und emittierter Photonenenergie, von räumlichen und zeitlichen Abhängigkeiten sowie von der Abhängigkeit der Fluenz eines Pumplasers, welcher einen Isolator-Metallübergang anregt, werden diskutiert. Multimodale Studien ermöglichen die Beobachtung von Quantenmaterialien mit verschiedenen experimentellen Techniken, wie Röntgenbildgebung, Röntgenabsorptionsspektroskopie, Röntgenemissionsspektroskopie, (resonanter) Röntgendiffraktion, resonanter inelastischer Röntgenstreuung (RIXS) und winkelaufgelöster Photoemissionsspektroskopie (ARPES).

Zunächst wird eine abbildende RIXS Methode vorgestellt, welche eine Transmissions-Fresnel-Zonenplatte verwendet um Weichröntgenabsorptionsspektroskopie mit Mikroskopie mit einer Auflösung von 1.8 µm zu kombinieren. Diese Methode wird in einer Studie des Isolator-Metallübergangs von Mikroquadraten, welche 30 µm × 30 µm klein sind und aus Vanadiumdioxid (VO₂) bestehen, angewendet. Abbildende Röntgenabsorptionsspektroskopie (XAS) zeigt, dass die Phasenübergangstemperatur an den Rändern der Quadrate im Vergleich zu den Zentren um 1.2 K verringert ist. Dies deutet darauf hin, dass sich die Eigenschaften von Quantenmaterialien durch Strukturierung auf der Mikroskala ändern können.

Weiterhin wird diese Methode auf abbildende Röntgenbeugung (XRD) übertragen, um das dotierte Titanatsystem $Y_{1-x}Ca_xTiO_3$ mit x = 0.37 zu untersuchen. Hierbei werden isolierende und metallische Phasen beobachtet, welche in gekrümmten, streifenförmigen Domänen über ungewöhnlich große Temperaturbereiche hinweg koexistieren. Diese Beobachtung steht in Zusammenhang mit einer variierenden chemischen Inhomogenität von etwa $x \pm 0.01$, die wahrscheinlich während des Kristallwachstums entstanden ist.

Auch Femtosekunden-Infrarot-Laserpulse können genutzt werden, um das elektronische System in Quantenmaterialien anzuregen und Isolator-Metall-Übergänge zu treiben. Für die Untersuchung der ultraschnellen Dynamik von Magnetit (Fe_3O_4) an einem FEL können Zonenplatten auch für die Methode des Time-to-Space Mapping verwendet werden, wobei eine Spanne des Zeitversatzes zwischen Pumplaser und FEL von mehreren Pikosekunden sowie eine Verteilung von Fluenzen gleichzeitig aufgezeichnet werden. Diese Methode kombiniert Informationen über Zeit, Raum und Pumpfluenz und kann in Zukunft für die Aufzeichnung von Einzelschussexperimenten entwickelt werden.

Schließlich wird die Methode der Photoelektronenspektrometrie zur Analyse von Röntgenstrahlung (PAX) weiterentwickelt. Diese Methode wandelt RIXS-Photonen mit Hilfe des photoelektrischen Effekts in Photoelektronen um. Sie wird genutzt um eine Probe aus der Familie der Hochtemperatursupraleiter mit hoher Energieauflösung zu untersuchen. Weiterhin ermöglicht PAX die simultane Messung einer Verteilung von Impulsüberträgen von Photonen auf die Probe. Der Bereich der Verteilung entspricht einem signifikanten Teil der ersten Brillouin-Zone in dem hier untersuchten System. Im Vergleich zu Gitterspektrometern ist ein PAX-Instrument viel kompakter, was Geld und Experimentierfläche spart. Der Erfolg der PAX-Methode führte zur Entwicklung einer speziellen Ultrahochvakuumkammer, die demnächst in Betrieb genommen wird und eine erhebliche Verbesserung der Photonenzählrate und der Energieauflösung sowie die Kombination mit ARPES verspricht.

Zusammenfassend werden in dieser Arbeit experimentelle Entwicklungen vorgestellt, welche die Untersuchung von Quantenmaterialien durch den Einsatz verschiedener Weichröntgenmethoden in Verbindung mit einer räumlichen Auflösung im Mikrometerbereich, einer Zeitauflösung im Bereich von 100 fs und einer Energieauflösung im Bereich von 100 meV ermöglichen. Darüber hinaus werden Konzepte zur Verbesserung dieser Energie- und Ortsauflösung um etwa eine Größenordnung vorgestellt. Die Weiterentwicklung der in dieser Arbeit beschriebenen experimentellen Werkzeuge wird ein tieferes Verständnis der Komplexität von Quantenmaterialien ermöglichen und uns als Gesellschaft in die Lage versetzen, Phänomene, die in Quantenmaterialien auftreten, nutzbar zu machen.

Preface

During my time as a doctoral student in the group FS-FLASH at the research institute Deutsches Elektronen-Synchrotron DESY, I participated in a number of projects that resulted in the publications listed below. Each of them profited from the contributions of many scientists from various institutes. The first five articles in which I am the first author constitute the core of my work and are included in this thesis. They are listed in the order in which they appear in this thesis.

Main Publications

 J. O. Schunck, F. Döring, B. Rösner, J. Buck, R. Y. Engel, P. S. Miedema, S. K. Mahatha, M. Hoesch, A. Petraru, H. Kohlstedt, C. Schüßler-Langeheine, K. Rossnagel, C. David, and M. Beye, Soft x-ray imaging spectroscopy with micrometer resolution, Optica 8, 156 (2021)

My contribution: I participated in the preparation of the beamtime and the experiment at PETRA III, contributed to the online analysis and was responsible for the final analysis of the data. I was responsible for writing the manuscript and communication with the editors and reviewers.

 J. O. Schunck, F. Döring, B. Rösner, J. Buck, R. Y. Engel, P. S. Miedema, S. K. Mahatha, M. Hoesch, A. Petraru, H. Kohlstedt, C. Schüßler-Langeheine, K. Rossnagel, C. David, and M. Beye, *Microstructure effects on the phase* transition behavior of a prototypical quantum material, Scientific Reports 12, 10464 (2022)

My contribution: I participated in the preparation of the beamtime and the experiment at PETRA III, contributed to the online analysis and was responsible for the final analysis of the data. I was responsible for writing the manuscript and communication with the editors and reviewers.

[3] J. O. Schunck, R. Y. Engel, P. Erberk, M. Scholz, S. Marotzke, R.-P. Wang, A. Jeromin, T. F. Keller, M.-J. Huang, M. Hoesch, F. Döring, C. David, A. C. Komarek, C. Schüßler-Langeheine, and M. Beye, *Stripes from chemical inhomogeneity in floating-zone grown rare-earth titanates*, in preparation (2025)

My contribution: I participated in the preparation of the beamtime and the experiment at PETRA III itself, contributed to the online analysis and was responsible for the final analysis of the data. I was responsible for writing the manuscript and communication with the editors and reviewers.

[4] J. O. Schunck, P. S. Miedema, R. Y. Engel, S. Dziarzhytski, G. Brenner, N. Ekanayake, C.-F. Chang, P. Bougiatioti, F. Döring, B. Rösner, C. David, C. Schüßler-Langeheine, and M. Beye, Simultaneous mapping of the ultrafast time and fluence dependence of the laser-induced insulator-to-metal transition in magnetite, Structural Dynamics 12, 024302 (2025)

My contribution: I participated in the preparation of the beamtime and the experiment at FLASH, contributed to the online analysis and was responsible for the final analysis of the data. I was responsible for writing the manuscript and communication with the editors and reviewers.

[5] J. O. Schunck, J. Buck, R. Y. Engel, S. R. Kruse, S. Marotzke, M. Scholz, S. K. Mahatha, M.-J. Huang, H. M. Rønnow, G. Dakovski, M. Hoesch, M. Kalläne, K. Rossnagel, and M. Beye, A compact approach to higher-resolution resonant inelastic x-ray scattering detection using photoelectrons, New Journal of Physics 26, 053008 (2024)

My contribution: I coordinated the preparation and experimental efforts, participated in the experiment at PETRA III itself, contributed to the online analysis and was responsible for the final analysis of the data. I was responsible for writing the manuscript and communication with the editors and reviewers.

Additional Publications During the time of my doctoral studies I have furthermore contributed to other experiments, which are not a main part of this thesis and resulted in the following publications, listed in chronological order:

[6] S. Dziarzhytski, M. Biednov, B. Dicke, A. Wang, P. S. Miedema, R. Y. Engel, J. O. Schunck, H. Redlin, H. Weigelt, F. Siewert, C. Behrens, M. Sinha, A. Schulte, B. Grimm-Lebsanft, G. S. Chiuzbăian, W. Wurth, M. Beye, M. Rübhausen, and G. Brenner, *The TRIXS end-station for femtosecond time-resolved resonant inelastic x-ray scattering experiments at the soft x-ray free-electron laser FLASH*, Structural Dynamics 7, 054301 (2020)

My contribution: I participated in the experiment at FLASH and contributed to the online analysis. I contributed to the manuscript.

[7] R. Y. Engel, P. S. Miedema, D. Turenne, I. Vaskivskyi, G. Brenner, S. Dziarzhytski, M. Kuhlmann, J. O. Schunck, F. Döring, A. Styervoyedov, S. S. Parkin, C. David, C. Schüßler-Langeheine, H. A. Dürr, and M. Beye, *Parallel Broadband Femtosecond Reflection Spectroscopy at a Soft X-Ray Free-Electron Laser*, Applied Sciences 10, 6947 (2020)

My contribution: I participated in the experiment at FLASH and contributed to the online analysis. I contributed to the manuscript. [8] X. Wang, R. Y. Engel, I. Vaskivskyi, D. Turenne, V. Shokeen, A. Yaroslavtsev, O. Grånäs, R. Knut, J. O. Schunck, S. Dziarzhytski, G. Brenner, R.-P. Wang, M. Kuhlmann, F. Kuschewski, W. Bronsch, C. Schüßler-Langeheine, A. Styervoyedov, S. S. P. Parkin, F. Parmigiani, O. Eriksson, M. Beye, and H. A. Dürr, Ultrafast manipulation of the NiO antiferromagnetic order via sub-gap optical excitation, Faraday Discussions 237, 300–316 (2022)

My contribution: I participated in the experiment at FLASH and contributed to the online analysis. I contributed to the manuscript.

[9] H. Rottke, R. Y. Engel, D. Schick, J. O. Schunck, P. S. Miedema, M. C. Borchert, M. Kuhlmann, N. Ekanayake, S. Dziarzhytski, G. Brenner, U. Eichmann, C. von Korff Schmising, M. Beye, and S. Eisebitt, *Probing electron and hole colocalization by resonant four-wave mixing spectroscopy in the extreme ultraviolet*, Science Advances 8, eabn5127 (2022)

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My contribution: I participated in discussions on the data evaluation and the theoretical modelling. I contributed to the manuscript.

[11] N. Thielemann-Kühn, T. Amrhein, W. Bronsch, S. Jana, N. Pontius, R. Y. Engel, P. S. Miedema, D. Legut, K. Carva, U. Atxitia, B. E. van Kuiken, M. Teichmann, R. E. Carley, L. Mercadier, A. Yaroslavtsev, G. Mercurio, L. Le Guyader, N. Agarwal, R. Gort, A. Scherz, S. Dziarzhytski, G. Brenner, F. Pressacco, R.-P. Wang, J. O. Schunck, M. Sinha, M. Beye, G. S. Chiuzbăian, P. M. Oppeneer, M. Weinelt, and C. Schüßler-Langeheine, *Optical control of 4 f orbital state in rare-earth metals*, Science Advances 10, eadk9522 (2024)

My contribution: I participated in the experiment at FLASH and contributed to the online analysis. I contributed to the manuscript.

[12] S. Marotzke, R.-P. Wang, R. Y. Engel, J. O. Schunck, and Martin Beye, Timeresolved soft X-ray methods on solids with the MUSIX endstation – Recent upgrades for geometric flexibility, Journal of Physics: Conference Series, in press (2025)

My contribution: I participated in the experiment at FLASH and contributed to the online analysis. I contributed to the manuscript.

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1 Introduction

He who sees things grow from the beginning will have the best view of them...

Aristotle

If we delve deeper and deeper into the matter around us, we ultimately encounter some of its smallest constituents: molecules, atoms, electrons and nuclei. In this quantum world, everything is determined by the laws of quantum mechanics: particles behave like waves, electrons are bound on quantized energy levels of their atoms and particles may tunnel through potential barriers. If several atoms are combined, new properties may arise, like the ability to absorb visible light that causes dye molecules to appear colourful to us. Adding even more atoms to form a crystal, the collective response of the electrons in bands may e.g. give it insulating or conducting properties and make it look transparent or opaque. If the electron spins align, a solid can become magnetic. Moreover, quantum systems can exist in superpositions — simultaneously holding multiple possible states — and entanglement links particles so that a change in one instantly affects its partner regardless of the distance between them.

Every new layer of complexity adds new laws that need to be understood to describe new phenomena that emerge [13]. And even though everything is subject to the same set of fundamental concepts, it would be hardly possible to use these fundamental concepts, developed by observing systems of a few particles, to explain much more complex systems [13].

At the beginning of the last century, the first quantum revolution marked the transition from the observation of quantum mechanical principles to their understanding. One example is the wave-particle duality. It describes the idea that particles (e.g. electrons) may behave like waves and enables the understanding of chemical interactions and the description of semiconductors through electronic wave functions. This fundamental understanding is what drives the computer-chip industry [14]. The contrary principle that light waves may behave like particles enabled the explanation of the photoelectric effect [15], awarded with the Nobel Prize to Einstein in 1921 [16]. Only with the concept of the photon, the laser, arguably one of the most versatile tools at our disposal, could be invented. These examples show how, as a consequence of the first quantum revolution, the understanding of quantum mechanics impacts our society and shapes the Information Age [17]. One common theme of technological applications is to make systems smaller and smaller, which has inevitably lead us to devices at the atomic and nano-scale where quantum effects are ubiquitous [18]. It is proposed that we now stand at the verge of a second quantum revolution, which describes the transition from the understanding of quantum mechanical principles to their control and encompasses simultaneous advancements in several fields, for instance quantum computing, quantum information technology and quantum materials.

A brief historical review of quantum materials can help to understand how this relatively new classification emerged. The kinds of materials which we nowadays refer to as quantum materials accompany humanity already for more than 2500 years: the magnetic properties of materials (e.g. magnetite (Fe_3O_4)) already sparked interest of ancient Greek philosophers [19]. In the 1930s and 1940s, Verwey discovered that magnetite in fact has an insulator-to-metal transition (IMT) [20, 21]. Soon it was discovered that other systems, like vanadium oxides and titanium oxides also exhibit this phenomenon [22], which was later found to occur due to strong electron correlations [23, 24]. These materials since have served as model systems for numerous studies of insulator-to-metal transitions in strongly correlated electron systems [25-28]. In the 1980s, the discovery of high-temperature superconductivity [29], awarded with a Nobel Prize to Bednorz and Müller in 1987 [30], caused a surge of research interest [31]. In the past 20 years, the discovery of interesting phenomena in condensed matter systems accelerated: The discovery of graphene [32] (Nobel Prize 2010 to Geim and Novoselov [33]), which is a system of sp^2 electrons and thus not a classical candidate for a strongly correlated material, and its unique properties sparked a growing interest in new topological materials, like topological insulators which are insulating in the bulk and possess a conductive layer at the surface, resulting in another Nobel Prize in 2016 to Thouless, Haldane, Kosterlitz [34]. This evolution made it clear that the emergent properties of matter are not restricted to only the classical strongly correlated systems and a broader term was needed: quantum materials. Starting in the 2010s, the term has gained in popularity, as reflected by the increasing number of publications and citations concerning quantum materials shown in Figure 1.1.



Figure 1.1: Publications (blue) and citations (red) related to quantum materials. Results were obtained by searching the database 'scopus' (https://www.scopus.com/) using the appearance of the terms 'quantum material' and 'quantum materials' in the fields keywords, title and abstract. Data from [35].

Quantum materials possess the commonality that their properties are governed by electron-electron and electron-lattice interactions [36-42]. The class of quantum materials encompasses the 'traditional' strongly correlated systems, like 3dtransition-metal oxides and high-temperature superconductors many of which have been studied for several decades [43–48]. Also two-dimensional systems, like (twisted bilayer) graphene [49], Van-der-Waals materials [50] and topological materials [51-53, which have gained in scientific interest more recently, exhibit strong correlations and phenomena, like IMTs, topological effects and superconductivity. While any object is governed by quantum mechanics, as it is made up of quantum objects like electrons, protons and neutrons, quantum materials possess emergent phenomena which result from many-body interactions of a host of different degrees of freedom. These include for example spin, orbit, charge, lattice and potentially topology as well as their interactions. This complexity of governing factors leads to a delicate energy landscape with potentially multiple close-lying ground states so that several quantum phases can be found in a single material. Even small changes of exterior parameters like temperature, strain, pressure, doping, external fields, etc. may drive the system into a different state, leading to a competition between phases (like antiferromagnetism and superconductivity in high-temperature superconductors [29, 48) and phase transitions (like insulator-to-metal transitions (IMTs) [46]). If two energetic minima are close to one another, two or more phases may even coexist forming phase-separated states [54]. In this case, a full description would entail a study of the individual phases to analyse the properties of each state, but also all coexisting states at the same time to study potential interactions.

This richness of interesting phenomena promises advancements for our society. For example, they can increase the efficiency of our energy grid: The Korea Electric Power Corporation (KEPCO) completed a first implementation of high-temperature superconducting cables into the public power grid in Korea [55]. Another example involves the use of thin-films containing vanadium dioxide (VO₂) which have an IMT close to room temperature. Thermochroic window coatings of VO₂ can automatically and reversibly turn windows opaque if they are heated by direct sunlight - and keep the interior cool [56]. The same material can also be used in small electronic devices, like infrared sensors, transistors or electric switches [28, 57]. If we continue to strive for a better understanding of these systems, maybe recipes for an even better performance can be derived.

Appropriate experimental tools are needed that provide enough flexibility and possible observables to study a particular system. In the past, the required tools were provided by lasers which kicked off the first quantum revolution in the 1960s and continue to be one of the most important tools in the scientists toolbox until today. In this context, the importance of developing new methods for characterization has been recognized by several Nobel Prizes [58–61]. Nowadays, scientist's tools are more diverse than ever before and even more selective tools are at our disposal. When the different degrees of freedom in quantum materials become interlinked, it can be experimentally challenging to identify which one plays the dominant role in the formation of a certain state or phase [42]. In addition, quantum materials typically consist of several elements that can contribute in different ways to the emergent properties. One famous example are the cuprate high-temperature superconductors which consist of copper-oxygen planes separated by other elements. The copper-oxygen planes are characterized by strong electron correlations and antiferromagnetic super-exchange interaction [62] and are therefore deemed especially important for the functionality of cuprates [48].

X-rays allow probing solids on atomic length scales and their electrons in core levels, bound deeply in the atoms [63]. Synchrotron sources provide X-ray beams with high spectral brightness, photon energy tunability and adaptive focusing capabilities. By using free-electron lasers (FELs), additionally atomic and electronic time scales of pico- and femtoseconds can be accessed [64–68]. At synchrotron radiation sources, the incident photon energy can be tuned to match a specific absorption edge in the sample. Addressing core resonances in this way yields element selectivity, which allows to study a particular species in quantum materials consisting of several elements. To return to the example of high-temperature superconducting cuprates, working at the 2p absorption edge of copper allows to probe the physics and low-energy spin, lattice, charge and orbital excitations in the copper-oxygen planes [42]. In this way, X-rays enable one to study how each constituent element contributes to the properties of a particular quantum material. This selectivity can even be extended to e.g. magnetic or oxidation states.



Figure 1.2: Energies for atomic K, L_3 and M_4 absorption edges in the soft X-ray energy range. Inspired by [69]; data from [70].

In contrast to other probes, X-rays present a unique combination of element and site selectivity, bulk sensitivity and small focusing capability: Electrons generally have much shorter penetrations depths and can only be somewhat bulk sensitive at very high (tens of keV) energies. Neutrons, on the other hand, have a generally rather low interaction cross section with matter. This, combined with the fact that neutron beams are large, means that samples need to be much larger than in X-ray experiments (which is not feasible for every sample system).

Within the realm of X-rays, generally one distinguishes between two main spectral regions: Soft X-rays have a photon energy in the range from about 300 eV to 2000 eV, and hard X-rays above 5000 eV^1 , while the intermediate range is also referred to as tender X-ray range. Corresponding wavelengths reach the atomic bond distance in the hard X-ray regime. The soft and hard X-ray regimes are different

¹The energy values given here are only approximate may be defined slightly different in different fields or literature.

from one another concerning several aspects. Penetration depths of soft X-rays are for example on the order of $1 \, \mu m$ or below for solids or about $1 \, cm$ in air under atmospheric conditions [47]. Therefore, sample environments providing ultra-high vacuum (UHV) conditions are needed, which generally complicates experiments. In contrast, when working with hard X-rays, samples can be exposed to air. Figure 1.2 shows atomic absorption edge energies for the K-, L_3 - and M_4 -shells. The soft X-ray range encompasses the 1s core levels of the so-called elements of life C, N and O, the 2p levels of the 3d transition metals which are constituents of many quantum materials and the 3d levels of catalytically important elements such as Ru, Rh and Pd. Exciting electrons of these core levels with soft X-rays is especially fruitful for two reasons: These levels present the sharpest core levels with the smallest amount of lifetime broadening of the respective elements [71] and at the same time allow for electronic dipole transitions into unoccupied valence states (with the transitions $1s \rightarrow 2p, 2p \rightarrow 3d, 3d \rightarrow 4f$). Therefore, if one wants to reach the highest chemical selectivity (e.g. to differentiate between different oxidation states of the same element), it is advantageous to work in the soft X-ray range at the cost of more complicated experimental setups under UHV conditions.

This selectivity of soft X-rays applies to a range of spectroscopic techniques: X-ray absorption spectroscopy (XAS) can be used to probe the unoccupied density of states (DoS) [44, 72], X-ray photoelectron spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES) measure electron binding energies and the occupied electronic band structure in solids [45, 73–76], resonant X-ray diffraction (RXD) is useful to probe structure as well as ordering of charge or spins [77] and resonant inelastic X-ray scattering (RIXS), unifying both absorption and emission, studies element-specific excitations including vibrational, magnetic, orbital, charge, and core excitations [42, 62, 78–80]. As it is also a scattering method, it can measure the dispersion of phonons, magnons and plasmons in energy-momentum space. These techniques, which are important to the content of this thesis, will be discussed in detail in chapter 2.

The success of **RIXS** for the study of quantum materials is largely determined by the development of adequate instrumentation. **RIXS** experienced a synergistic evolution of methodological improvements and scientific breakthroughs, especially in the field of strongly correlated materials (like the cuprates) [42]. One challenge in RIXS is to resolve desired low-energy excitations on an energy scale of tens of millielectronvolt at soft X-ray photon energies of typically several hundred electron volt [42, 81]. Considering that a typical temperature for phase transitions in quantum materials is $T \approx 100 \,\mathrm{K}$, the associated energy scale of $k_B T \approx 10 \,\mathrm{meV}$ and time scale of $\hbar/(k_B T) \approx 100$ fs are important targets [42]. This is also the energy resolution required to resolve the opening of the superconducting gap in high-temperature superconducting cuprates, which is the class of materials that RIXS has probably been applied to the most. Nowadays, high resolution RIXS instruments are becoming more versatile and available at many different facilities around the world [82-88]. A variety of methods exist that can measure similar information as RIXS, each with different strengths and limitations. These are discussed in greater detail in chapter 2.7.1. In short, inelastic neutron scattering (INS) can study magnetic excitations with very high energy resolution, but cannot be focused onto small samples. Also

electron energy loss spectroscopy (EELS) can achieve similarly high energy resolution, but is limited by the electronic mean free path to interactions with the sample surface. Raman spectroscopy in the ultraviolet (UV), visible and infrared (IR) spectral regions studies hybridized valence bands and therefore probes a mixture of the response of constituent elements.

Quantum materials also harbour the experimental challenge that they might not respond in a spatially homogeneous manner if domains of two or more phases coexist. The result is a need for probes that are designed to study electronic structure and properties of quantum materials together with the spatial arrangement of phases, as well as their evolution if external parameters are changed. This is a challenge for the traditional way in which X-ray spectroscopy methods and the other techniques outlined above are measured, where usually the signal from the entire illuminated spot is integrated. The simplest approach to apply any X-ray spectroscopy method to an inhomogeneous sample would be to make the X-ray focus as small as possible and scan it across the sample. However, this causes several complications: Typical soft X-ray focusing optics are challenging to manufacture with a surface roughness that allows focusing to sizes better than a few micrometres, especially in the horizontal dimension where the source size is much larger at third generation synchrotron sources. Second, small focusing increases the radiation dose absorbed by the sample, which may be damaged in the process. Lastly, if the previous issues can be circumvented, raster-scanning of the sample position is required to gain information on the spatial dependence of the observed signal which requires potentially long measurement times and high stability of the experimental setup and the sample itself.

A noteworthy mention of a technique that combines high spatial resolution with electronic structure information is scanning transmission X-ray microscopy (STXM). STXM is a technique which is able to measure X-ray absorption spectra with a spatial resolution on the level of tens of nanometers [89–91]. Using absorption contrast, STXM can also measure elemental maps of samples. However, since STXM measures in transmission, samples thicknesses should be in the sub-micron range [91]. The spatial resolution can even be increased beyond 10 nm [92–94]. To provide the required stability to scan with an accuracy of a few tens of nanometers is not easy, but has been achieved using laser-interferometry [95]. Also (lensless) soft X-ray holography [96] and ptychography are related techniques that can be applied to thin transmission samples. With these methods, e.g. coexisting phases in vanadium dioxide (VO₂) were studied [97].

For RIXS, it is not straightforward to increase the parameter space for extensive scans of sample position, as it is a photon-hungry technique and scanning additional dimensions is not feasible with the current way RIXS is measured. One central topic to this thesis is the RIXS imaging approach, developed for the study of microscopic domains in quantum materials. By parallelising acquisition of a broader range of incident energies, it reliefs the constraint count rate of RIXS. In comparison to STXM, spatial resolution is sacrificed for the benefit of increased flexibility concerning choice of suitable samples and applicable soft X-ray methods. Several different techniques, like XAS, XES, RXD, RIXS or XRD can be realized with minimal setup variation, yielding a multimodal setup. Furthermore, it can be applied not only to transmis-

sion but also to bulk samples which greatly enhances the choice of systems that can be investigated. The parameters that can be studied are dependencies on spatial coordinates as well as on incident and emitted photon energies. If this method is used at FELs, additionally femto- and picosecond time-dependences as well as pump-laser fluence dependence can be investigated, making this method multidimensional.

At his opening talk of the conference 11th international conference on inelastic X-ray scattering (IXS2019), entitled 'Inelastic X-ray Scattering: Past, present and future', John Hill, former director of NSLS-II, discussed the future of soft X-ray RIXS on solids and arrived at a similar conclusion. In his outlook, he defined three Goals for the field [98]:

1. Add spatial resolution.

2. Combine **RIXS** with **ARPES**.

3. Achieve an energy resolution of $\Delta E = 1 \text{ meV}$.

All of these three items are addressed by the methodological developments presented in this thesis: Goal 1 is addressed with the RIXS imaging setup. Paper I [1] describes this setup which combines RIXS (and more generally also XAS and X-ray emission spectroscopy (XES)) with a spatial resolution of currently about $2 \mu m$ through the use of an off-axis Fresnel zone plate for the study of coexisting phases. In Paper II [2], the RIXS imaging setup was used to track the local progression of the thermally driven IMT in VO₂ microstructures. A closely related setup, used in the study presented in Paper III [3], transfers the $2 \mu m$ spatial resolution to full-field diffraction imaging for a study of the spatial arrangement and thermal evolution of millimetre-scale stripe domains arising from chemical inhomogeneity in $Y_{1-x}Ca_xTiO_3$.

At FELs, Goal 1 can be extended to the time domain. In a similar zone plate setup as discussed before, a time-to-space mapping setup is developed in Paper IV [4] for time-resolved pump-probe experiments at FELs. In this setup, an off-axis Fresnel zone plate in combination with the appropriate arrangement of IR pump and X-ray probe beams, allows, in principle, to measure delay and fluence² dependences in a single pump-probe cycle. We used this setup to study the ultrafast light-induced phase transition of a magnetite (Fe₃O₄) thin-film, probing the excitation with RXD at the iron L_3 -edge.

Goal 2 and Goal 3 are both addressed with a method termed photoelectron spectrometry for the analysis of X-rays (PAX), which is the second central topic of this thesis. PAX presents a new way to measure RIXS by converting scattered X-rays to photoelectrons. Bringing the very high energy resolution of an electron spectrometer to RIXS is explored in Paper V [5]. A new experimental chamber is in development, targeted to make PAX more efficient in the future and designed to measure PAX in conjunction with ARPES on the same sample spot and without breaking the chamber vacuum.

²Energy per area.

2 Soft X-ray Spectroscopy of Quantum Materials

This chapter gives an overview of the phenomena in quantum materials relevant to this thesis (insulator-to-metal transition in section 2.1.1 and phase separation in section 2.1.2) and discusses soft X-ray radiation sources (section 2.2) as well as the soft X-ray spectroscopy and diffraction techniques used in Papers I-V (sections 2.3 to 2.8).

2.1 Phenomena in Quantum Materials

Quantum materials exhibit a suite of extraordinary phenomena, many of which are not subject to the studies that compose this thesis. Those that are important to this thesis, insulator-to-metal transitions (IMTs) and phase separation, are described in the following two sections, along with examples for X-ray methods that are wellsuited to investigate these phenomena. The methods are then described in detail in later sections of this chapter. High-temperature superconducting cuprates, which are important for chapter 4, are discussed in section 4.1.

2.1.1 Insulator-to-Metal Transitions

For quantum materials, many examples of systems exist which can transition between insulating and metallic properties [46]. Often, these systems are insulating with a half-filled valence band at the Fermi level, which is a contradiction according to classical band theory. Both Mott and Peierls presented two different explanations for this phenomenon and why such systems can transition into a metallic state. Their contradicting models gave rise to the so-called Mott-vs-Peierls competition. Vanadium dioxide (VO₂), which is subject to the experiment described in Paper II [2] was one of the first materials in which this competition was investigated (see e.g. [24, 100, 101]).

Many more classifications for insulators which exist (e.g. charge-transfer insulator and Anderson insulator) are beyond the scope of this thesis. A thorough description of different cases of IMTs can for example be found in [25].

An instructive description of Mott insulators can for example be found in [45]. If N hydrogen atoms are arranged in a periodic chain, the overlap of wave functions leads to the formation of an energy band of bandwidth B (see Figure 2.1a). This band contains 2N states because of two possible electron spin configurations. Were all states occupied, such a solid would be an insulator or semiconductor. In the example of hydrogen atoms constituting the solid, the band is half-filled, which would lead to a metallic state according to band theory. If one imagines that the hydrogen atoms



Figure 2.1: Mott and Peierls models of metallic and insulating phases. Panel a: In the metallic state as described by Mott, the system has a large bandwidth B and smaller electron Coulomb repulsion U screened by delocalization of electrons. Panel b: narrow bands and large Coulomb repulsion leads to localization of electrons making the system insulating. Panel c: In the metallic phase according to Peierls, a regularly spaced array of atoms leads to a parabolic dispersion relation which is filled up to the Fermi level (green). A pairing of atoms (panel d) allows the system to gain energy upon lowering the temperature. This introduces a band gap at half the Brillouin zone and effectively doubles the unit cell. Inspired by [45, 99].

are pulled apart from one another, the orbitals become increasingly localized around the nuclei (Figure 2.1b). Each orbital is singly occupied, since double occupancy is energetically too expensive due to the Coulomb repulsion U between the electrons. Two forces thus compete with each other: the Coulomb energy that leads to electron localization and the kinetic energy which the system tries to minimize by delocalizing electrons. According to the uncertainty principle $\Delta x \Delta p \geq \hbar/2$ (with the reduced Planck constant \hbar), a large uncertainty in space Δx leads to a smaller uncertainty in momentum Δp and the kinetic energy can be lowered with a smaller energy spread. In systems with a large bandwidth (B > U), the Coulomb interaction is well-screened, the kinetic energy dominates and correlations can be approximated by an average potential. Such a metallic system (Figure 2.1a) is well-described by a oneelectron theory based on Bloch's theorem. If bands are narrow (B < U), Coulomb interactions dominate and the system is an insulator at half-filling (Figure 2.1b). For example, the 3*d* orbitals are generally localized, leading to strong Coulomb interactions in 3*d* transition metal oxides, which are therefore often classified as Mott insulators.

Contrarily, the Peierls distortion describes an IMT driven by a lattice rearrangement. If one considers a one-dimensional chain of atoms, the metallic state is characterized by a regularly spaced array of atoms that lead to a parabolic dispersion relation (Figure 2.1c). If the temperature is lowered, a lattice distortion occurs that leads to a pairing of atoms within the chain, effectively doubling the unit cell and causing a band gap to open in the dispersion relation at the wave vector corresponding to half of the first Brillouin zone (Figure 2.1d) [99].



Figure 2.2: Temperature-dependent resistivity and resistance curves for heating (red) and cooling (blue) of the insulator-to-metal transition compounds investigated in this thesis. The VO₂ (50 nm thin-film on Al₂O₃) and $Y_{0.63}Ca_{0.37}TiO_3$ (single crystal) data were measured on the same samples used during the measurements presented in the respective publications [1–3]. The Fe₃O₄ (40 nm thin-film on Co₂TiO₄) data is taken from [102] but was also measured on a sample similar to the one used in [4].

Figure 2.2 shows the change of electrical resistivity during an IMT for three different systems that are investigated in this thesis. VO_2 and Fe_3O_4 are two of the longest-known IMT systems [20, 22] that have both been studied extensively throughout the past decades [26–28]. From a comparison of the different panels in Figure 2.2, one can see that $Y_{0.63}Ca_{0.37}TiO_3$ has an especially peculiar phase transition as it is metallic at low temperatures and insulating at higher temperatures (in contrast to VO_2 , Fe_3O_4 and many other quantum materials that show an IMT) and because the resistivity hysteresis extends across a much larger temperature range. Depending on the changes that these systems experience, different methods, providing different kinds of contrast, can be used to track the phase transition. For example, in VO_2 , which is subject to Paper II [2] (section 3.2.2), the change of the electronic structure during the IMT can be tracked using X-ray absorption

spectroscopy (XAS) [103] and changes of the crystal structure can be studied with X-ray diffraction (XRD) [104]. In magnetite, studied in Paper IV [4] (section 3.3), the IMT is accompanied by an order-to-disorder transition that can be tracked by means of resonant X-ray diffraction (RXD) [105, 106]. Of course, the methods mentioned here are the examples used in this thesis, but many techniques, featuring X-rays and also other probes, can be used to study these systems. Lastly, XRD is a well-suited method to probe the structural changes that occur during the IMT in $Y_{0.63}Ca_{0.37}TiO_3$, studied in Paper III [3] (section 3.2.3).

2.1.2 Phase Separation

The complex energy landscape that forms quantum materials can lead to multiple states that are very close to each other in energy [107]. In consequence, smallest changes of internal (doping, defects, strain etc.) or external parameters (temperature or electric or magnetic fields) may change the favoured ground state [108]. Furthermore, the transition of one phase to the lowest energy phase is obstructed by a kinetic energy barrier. On microscopic length scales, these factors can lead to the coexistence of two or more phases. Macroscopically, phase coexistence can lead to the emergence of some of the intriguing phenomena that quantum materials are known for. One example are the cuprates in which competition and coexistence of superconductivity and periodic charge oscillations in the form of charge-density wave is thought to play a crucial role in the occurrence of high-temperature super-conductivity [109–113].



Figure 2.3: Phase separation and percolation of a metallic domain. Coexistence of insulating (white) and metallic (blue) domains. Left panel: As long as there is no connecting path from one end of the system to the other, the macroscopic state is the insulating one. Right panel: By only switching the phase in a few locations, a connected metallic path from one end to the other forms, leading to a macroscopic metallic behaviour along the corresponding direction. Inspired by [114].

Figure 2.3 shows metallic islands (blue) that exist within an insulating phase (white). If the islands are not interconnected (left panel), a macroscopic measurement of the resistivity would yield an insulating state. However, just switching in-

sulating areas to metallic ones locally in a few places (which is energetically cheaper than switching the entire sample) can create a metallic path through the sample which would lead to the measurement of a macroscopic metallic state. This exemplifies that knowledge of the distribution and properties of coexisting phases harbours the chance for new applications. Only through the study of the individual phases and their interplay, full understanding of phase-separated materials and their functionality can be obtained. However, this is challenging because a sufficient spatial resolution of an experimental method, as well as an observable that yields contrast to visualize the phases and their distribution are required.

X-ray spectroscopy or diffraction can utilize different responses of coexisting phases in, respectively, the electronic or crystallographic structure as contrast. Exploring new methods to combine the contrast of these methods with the required spatial resolution is one goal of this thesis, see Papers I-III [1-3] in chapter 3.

2.2 Soft X-ray Radiation Sources

The soft X-ray radiation used to obtain the experimental results presented in this thesis was produced from two different kinds of sources: synchrotron radiation sources and free-electron lasers (FELs). The fundamentals regarding creation of synchrotron and FEL radiation from relativistic electron bunches can be found elsewhere, for example in [63, 115, 116]. The differences in radiation properties, experimental setups and goals between these two types of facilities will be described in this section.

Although synchrotrons produce X-ray pulses with a full width at half maximum (FWHM) duration of typically 50 ps to 100 ps [63], soft X-ray spectroscopy experiments at synchrotron sources typically do not make use of this picosecond pulse duration. Instead, a sample of interest is usually investigated under 'static' conditions in the sense that external parameters, like sample temperature or fields, are kept as stable as possible while a dataset is acquired. Changing these parameters is typically done in between measurements. Before a data set is taken, one waits for the sample to equilibrate. Synchrotrons are generally well-suited for such static measurements because they provide stable beam conditions. For example, the top-up filling mode keeps the electron ring current stable to about 1% or better [63]. Such a static experiment also poses relatively relaxed conditions for the detector read out. For the experiments presented in this thesis that were measured at a storage ring (Papers I, II, III, V), two-dimensional detectors were operated with exposure times typically ranging from one second to one minute.

FELs provide much shorter and more intense pulses with variable duration (but generally on the order of 50 fs), which each can contain as many photons as a synchrotron radiation source delivers in one second [68]. A quantitative comparison of the spectral brightness between FLASH, PETRA III and the future fourth generation synchrotron source PETRA IV is shown in Figure 2.4. The spectral brightness

¹Since the electrons oscillate along the sinusoidal trajectory and the photons do not, electrons will progress less far along the undulator axis. The resonance condition to achieve microbunching is realized when the path difference 'setback' which electrons experience in a single undulator period equals the wavelength of the radiation [67].



Figure 2.4: Spectral brightness of FLASH, PETRA III and PETRA IV. The left and right panels respectively show the spectral brightness for a single pulse and the spectral brightness averaged over one second. For FLASH, spectral brightness data of the fundamental, the third harmonic and seeded operation are shown (see also main text). For PETRA III, the spectral brightness in the soft X-ray range shows data for the UE65 undulator used at the soft X-ray beamline P04 and for the hard X-ray region, data of a 5 m U29 undulator (as e.g. used at beamline P10) is shown. Data from [117, 118].

is a measure to compare different X-ray sources by normalizing the emitted number of photons to time, energetic bandwidth and emittance in transverse directions. If the spectral brightness is only calculated for a single pulse, FELs are generally orders of magnitude brighter than synchrotron sources (see left panel in Figure 2.4 and also [120]). However, due to generally much higher repetition rates of synchrotrons, this differences is diminished if the average spectral brightness in one second is used as a measure (see right panel in Figure 2.4). Benefiting from a superconducting accelerator, the free-electron laser in Hamburg (FLASH) has a high average repetition rate of up to 5000 pulses/s with a high degree of coherence and provides photon energies in the range of approximately 25 eV to 300 eV [121]. Like most free-electron lasers around the world [67], FLASH uses the process of self-amplified spontaneous emission (SASE) to create the FEL radiation². This process is sketched in Figure 2.5. A more detailed description of the SASE process can be found e.g. in [123]. Essentially, the non-linear FEL amplification process is started from shot noise and

²It should be mentioned that FLASH was shut down in 2024 to upgrade FLASH1 to an externally seeded source, which will be commissioned in 2025 and 2026 [121, 122]. Seeding will improve the coherence, leading to a reduction of the spectral bandwidth, improve pulse-to-pulse stability and increase the spectral brightness, as shown in Figure 2.4.



Figure 2.5: The process of self-amplified spontaneous emission (SASE). Initially, the electron distribution in the bunch is only modulated by shot noise [119]. Spontaneously emitted photons start applying a potential on the electrons in longitudinal direction, thereby leading to the formation of microbunches (blue disks). In the exponential gain regime, electrons within a microbunch oscillate coherently, transferring energy to the electromagnetic field, thereby also increasing the degree of bunching. Saturation is reached when the energy of the electron bunch is decreased so far, that the undulator resonance condition¹ is not fulfilled any more.

eventually results in a random modulation of the energy spectrum and temporal structure of individual FEL pulses [68, 119, 124–128]. The Gaussian-shaped envelope of the spectral SASE modes typically has a bandwidth of approximately 1 % (FWHM) of the photon energy [129]. Furthermore, harmonics of the fundamental photon energy $E_{\rm ph}$, amplified by SASE, are produced [124, 130, 131]. The $n^{\rm th}$ harmonic radiates at a photon energy of $nE_{\rm ph}$. The third harmonic in particular is often used at FLASH to access energies above 300 eV, like the nitrogen or oxygen K- or transition metal $L_{2,3}$ -edges. The pulse energy content of the third harmonic is on the order of 0.5% in comparison to that of the fundamental [124]. Harmonics also occur at synchrotron beamlines, if undulators are used as insertion devices [116].

The short pulse duration of FELs makes these machines a suitable tool for timeresolved measurements. Commonly, a two-pulse pump-probe scheme is used: A first pulse (the pump) excites the system or triggers a certain process (e.g. magnetic switching or a phase transition) and after a (ultrashort) while, the second pulse (the probe) investigates the induced changes [68, 132–134]. These pump-probe cycles are repeated many times while changing the time delay which passes between pump and probe to obtain a picture of the full dynamics. Often, the pump pulse is an IR or optical pulse from a separate laser system and the probe pulse is from the FEL. The method used to probe the sample can be adjusted to the scientific question and the sample itself. To investigate the complex phenomena in quantum materials, spectroscopic probes like XAS, XPS, RIXS or RXD are especially well-suited, as discussed in the Introduction 1. The required temporal resolution to study ultrafast dynamics in solids is in the femtosecond to picosecond range, which corresponds to the time scales for the motion of electrons and nuclei. Detector readout speeds are much slower, but the temporal resolution will be determined by the durations of both pulses as long as a detector is only illuminated by a single probe pulse and is read out before the next pulse arrives, as well as by the relative arrival time jitter between both pulses. The latter can be reduced by synchronizing optical and FEL pulses [135].

There are many examples for time-resolved studies of quantum materials, summarized in these overviews: [39, 41, 128, 136–138]. The excitation of quantum materials with ultrafast laser pulses provides a different handle on emergent phenomena besides those commonly accessible in static experiments, like temperature, fields and pressure. With laser pulses, insulator-to-metal transitions can be induced [139–141] (as highly relevant for this work, see chapter 3.3), or hidden, non-equilibrium phases can be induced. A famous example is superconductivity induced by laser pulses [142]. The time-domain also presents a chance to distinguish between different driving forces of insulator-to-metal transitions based on different characteristic response times [143]. For example, the rearrangement of the lattice during a Peierls transition proceeds on the picosecond timescale, whereas an electronically driven Mott transition proceeds on the femtosecond timescale [143]. Concerning high-temperature superconductors, a central, long-standing question concerns the competition between charge order (CO) and superconductivity. In the time-domain, it has been found that pumping with 15 µm pulses enhances interlay transport and diminishes the CO [144].

2.3 Overview of Soft X-ray Spectroscopies

With spectroscopic techniques, light-induced electronic transitions in a material of interest can be studied. Physical properties of this material can be identified by observing the resulting transitions and their dependence on parameters like photon energy, temperature, sample composition, etc. The information obtained from the material are different depending on which electronic transitions are observed with different spectroscopic methods shown in Figure 2.6. During the process of X-ray absorption spectroscopy (XAS) (see section 2.4), the energy of the incident X-ray photon is used to promote an electron from a core level to either an unoccupied valence state, meaning that the electron does not leave the atom (resonant XAS) or, if the energy of the X-ray photon exceeds the electron binding energy significantly, the atom is ionized and the electron is removed from the atom. X-ray photoelectron spectroscopy (XPS) (see section 2.5) measures the energy of electrons which are ejected in this way and is thus able to directly measure the binding energy of electrons. Furthermore, the direction of electron emission can be used to measure the momentum of the emitted electron, allowing to infer information on the electronic band structure of a solid sample. This technique is called angle-resolved photoemission spectroscopy (ARPES).

The core hole, which is created during the absorption of a photon, is highly energetic and unstable and decays after a short lifetime of typically a few femtoseconds. This decay can occur radiatively or non-radiatively, as discussed later in more detail. Resonant inelastic X-ray scattering (RIXS), X-ray emission spectroscopy (XES) and resonant X-ray diffraction (RXD) study the radiative decay of this core hole by detecting the (re)emitted photon. The soft X-ray techniques discussed in this chapter possess an analogue in other regions of the electromagnetic spectrum, but this thesis will focus only on their application to the soft X-ray spectral range (approximately 300 eV to 2000 eV).

The probability P_{fg} that the incident photon of energy $\hbar\omega$ excites the electronic transition from a ground state $|g\rangle$ to a final state $|f\rangle$ is described by Fermi's golden rule, which describes one-electron processes, like XAS, XPS, and XES [72]:

$$P_{fg} \propto \left| \langle f | \hat{d} | g \rangle \right|^2 \delta \left(E_f - E_g - \hbar \omega \right) \tag{1}$$

Here, the dipole transition operator \hat{d} considers only dipole transitions that change the angular momentum quantum number l by ± 1 , which is a good approximation for the soft X-ray spectral range. Only in the hard X-ray regime, quadrupole and higher order transitions become relevant [72]. The squared matrix element in equation 1 yields the transition rate and the delta function $\delta (E_f - E_g - \hbar \omega)$ states that a transition only takes place, if the photon energy $\hbar \omega$ equals the difference between the energies of the final state E_f and the ground state E_g , thus essentially representing energy conservation. More complex spectroscopic processes, such as RIXS and RXD involving two photons cannot simply be described by applying Fermi's golden rule twice, but instead need to be described in a single process, which gives rise to the intermediate state interference (see section 2.7).

Koopmann's approximation states that the binding energy equals the negative energy of the orbital from which a photoelectron originates [145, 146]. While this



Figure 2.6: Level diagrams of different X-ray spectroscopy processes. The absorption of an X-ray photon (purple) creates a core hole (empty circle) and leads to the promotion of a core electron to the unoccupied valence in the X-ray absorption spectroscopy (XAS) or across the ionization potential (IP) in the X-ray photoelectron spectroscopy (XPS) process (filled circles). In resonant X-ray diffraction (RXD), the corevalence excitation decays when the excited electron recombines with the core hole, emitting a photon of the same energy as the incident photon (purple). In resonant inelastic X-ray scattering (RIXS) and X-ray emission spectroscopy (XES), an electron from an occupied valence state fills the core hole, resulting in the emission of another photon (blue) with an energy that is lower than that of the incident photon. The final state in RIXS is a low-energy, charge-neutral excitation, whereas that in XES is commonly an ionized state.

approximation describes a very intuitive picture for why photoelectron spectroscopy is rich in information, it immediately breaks down, once correlations between electrons are considered. When electrons in an atom are excited or an atom is ionized, the total energy of the system is raised and the remaining electrons in the atom will rearrange in order to lower its energy. This screening response is stronger if the atom is ionized as compared to a situation where the electron is excited to the conduction band, and the screening response is also much stronger if a core hole is created as compared to if a valence hole is created [147, 148]. Since the screening of the hole happens basically instantaneously, X-ray spectroscopy always measures the energy of the created final state. Thus, different techniques which result in a different final state will obtain a different result, even if the same electronic state was initially excited [147, 148].

2.4 X-ray Absorption Spectroscopy (XAS)

The conceptually simplest absorption experiment measures the transmission of a sufficiently thin sample as the ratio of incident intensity I_0 and transmitted intensity I_t . According to the Lambert-Beer law (equation 2), this ratio depends on the atomic density n_a , the photo-absorption cross-section σ_{abs} and the thickness x of the material. The absolute absorption cross-section σ_{abs} can be determined if the thickness of the sample is known and I_0 and I_t are measured [116, 149].

$$\frac{I_t}{I_0} = \exp(-n_a \sigma_{\rm abs} x) \tag{2}$$

The attenuation length (defined as the length after which incident radiation has been attenuated to 1/e) of soft X-ray radiation in solids is in the range of up to a few hundred nanometers [70] posing a constraint on the maximum thickness for transmission samples for soft X-ray experiments.

In the soft X-ray range between 300 eV and 2000 eV, the photon energy is sufficient to excite electrons in core levels. Performing a transmission experiment, a sudden rise in absorption efficiency of the sample can be observed at a particular photon energy, which is referred to as the absorption edge. Precisely at the energy of the edge, the energy of the photon is sufficient to excite an electron from a core level to the lowest unoccupied state, see Figure 2.6. Therefore, measuring the Xray absorption of a sample can be used to probe the unoccupied density of states (DoS), which is sensitive to various intrinsic and extrinsic influences. Examples are, first of all, the elements themselves, whose electrons have very different binding energies. Furthermore, changes in oxidation state, crystal lattice, external magnetic fields, temperature, etc. may affect the binding energy of core electrons and are thus measurable with X-ray absorption. In solids that are composed of several elements, this sensitivity of X-rays can be used to selectively probe the behaviour of a specific element of interest. The core hole which is created during the X-ray absorption process (see Figure 2.6) is generally unstable and therefore has a short lifetime. This means that corresponding absorption peaks are generally broad in energy (in comparison to features resulting from long-lived final states) and often the spectral resolution which can be achieved in an XAS experiment is limited by the lifetime broadening.

Besides transmission through a sample, yield methods also measure X-ray absorption by detecting the number of photons or electrons which are emitted from the sample upon absorption of an X-ray photon.



Figure 2.7: Electron yield (EY) and fluorescence yield (FY) for the K (green), L_3 (blue) and M_4 (red) shells of the first 92 elements. The FY in the soft X-ray spectral region (purple, from 300 eV to 2000 eV) ranges from less than one per mille to a few percent. The elements which have a K-, L_3 - or M_4 -edge in the soft X-ray range are named in Figure 1.2. Data from [70, 150, 151].

Fluorescence, the radiative decay of a core hole, is the minority channel in the soft X-ray region. Any electron from a higher shell, or the valence, may fill a core hole which was created during the absorption process. Total fluorescence yield (TFY) detects all of these fluorescence photons without discriminating their energy. This results in a rather simple setup and a generally decent count rate, even in the soft Xray region, which is less favourable for radiative processes as compared to the hard Xray region (see Figure 2.7). Partial fluorescence yield (PFY) measures the energy of fluorescent photons using a spectrometer downstream of the sample. This allows to obtain information on a single decay channel, enabling one to select e.g. a particular spin orientation or chemical state [72], but results in much lower count rates in comparison to TFY. Many different types of samples, like bulk single crystals, thin films or powders are suitable for fluorescence yield (FY) measurements and the probing depth corresponds to the penetration depth of soft X-rays (i.e. up to a few hundred nanometers). When performing a FY experiment, one implicitly assumes that the decay channels which contribute to the measured FY are proportional to the absorption cross-section. For most cases in the soft X-ray region this assumption is good, but e.g. at the *L*-edges of 3d transition metals, this assumption is wrong, and FY does not measure the true absorption [152]. Furthermore, self-absorption³, which depends on the concentration of the absorbing species, the photon energy, and the angles of incidence and emission, may influence FY measurements [152].

 $^{^{3}}$ The reabsorption of a fluorescent photon before it can leave the material

Therefore, care has to be taken if one wants to use FY measurements to determine the absorption cross-section [153-156].

The Auger-Meitner process is in competition with the fluorescent decay of a core hole: The energy which is released when the core hole is filled can be transferred to another, higher-lying electron, resulting in its ejection. Both the Auger-Meitner electron, as well as the initially ejected photoelectron can also collide with other atoms and eject secondary electrons of lower energy. The inelastic mean free path (IMFP) of electrons traversing a solid depends on the electron energy, but is generally on the order of below 1 nm up to 10 nm [157] (see also section 2.5 and Figure 2.9). Therefore, methods detecting electrons in the soft X-ray region are very sensitive to the surface and the first few layers of solids. Furthermore, care has to be taken that the sample, substrate, glue and sample holder are sufficiently conductive to prevent the build-up of any charge. Although electron yield (EY) measurements generally, and Auger-vield measurements specifically, are much closer to the 'true' absorption coefficient [152], saturation effects (related to the relative and material- and energy-dependent penetration depth of X-rays in comparison to the escape depth of electrons) may still occur, necessitating some additional considerations in order to infer the absolute absorption cross-section [158].

2.5 Photoelectron Spectroscopy (PES)

The method of photoelectron spectrometry for the analysis of X-rays (PAX), which is the topic of Paper V [5] in this thesis (see section 4.2), measures RIXS indirectly via an intermediate photoemission process, as previously outlined in the Introduction (chapter 1). Therefore, PES is introduced in this section with a focus on X-ray photoelectron spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES).

Photoelectron spectroscopy (PES) utilizes the photoelectric effect, which was explained by Einstein in 1905 [15] and awarded him the Nobel Prize in 1921. It is shown in Figure 2.8: A photon which is incident on a solid (left) can eject photoelectrons from the solid if the photon energy $\hbar\omega$ is higher than the sum of the binding energy of the electron E_B and the work function ϕ of the material. The work function is the energetic barrier between the Fermi level E_F and the vacuum level $E_{\rm vac}$ which the photoelectron has to overcome to escape from the surface [146], as also shown in Figure 2.8. If a spectrometer is used to measure the kinetic energy of the photoelectron, also the work function of the analyser has to be considered, which is in electrical contact with the sample [75]. The kinetic energy of the electron after ejection is then given by:

$$E_{\rm kin} = \hbar\omega - E_B - \phi \tag{3}$$

If a monochromatic light source is used, measuring the kinetic energy of the photoelectron yields a measure for the binding energy of the electron. Depending on the photon energy, different electronic levels can be accessed: Ultraviolet photoelectron spectroscopy (UPS) uses ultraviolet (UV) light (around 5 eV to 100 eV), which is suited to study the valence band. With X-ray photoelectron spectroscopy (XPS)



Figure 2.8: Schematic X-ray photoemission process of a thin silver (Ag) film. A photon with an energy of $\hbar \omega = 931 \,\text{eV}$ (purple) excites an electron of either the 3*d*-core (green) or 4d/5s-valence level (blue) of a silver sample. The photoelectron has to overcome the binding energy of the level it originates from and the work function ϕ . It leaves the atom once it crosses the vacuum level (E_{vac}) with a remaining kinetic energy that is given by equation 3. The measured kinetic energy distribution resembles the electronic structure of the sample closely. Inspired by [146].

using X-rays, on the other hand, the higher photon energies enable the investigation of deeper core levels (see also Figure 2.6), which are sensitive to the chemical state and the local chemical environment of the atoms, in addition to the study of valence states, as shown in Figure 2.8 for the valence and 3d core states of silver. The technique of using XPS specifically for chemical analysis of binding energies is also known as electron spectroscopy for chemical analysis (ESCA) [159, 160].

In contrast to XPS, angle-resolved photoemission spectroscopy (ARPES) utilizes not only energy conservation between photon and photoelectron to deduce information on binding energies, but also momentum conservation to measure the electronic band structure. The component of the photoelectron momentum parallel to the surface can be inferred directly from measurements of the photoelectron's kinetic energy and emission angle ϑ relative to the surface normal [146]:

$$\hbar \vec{k}_{\parallel} = \sqrt{2m_e \cdot E_{\rm kin} \cdot \sin^2\left(\vartheta\right)} \tag{4}$$

Here, m_e denotes the mass of the electron, and $\hbar \vec{k_{\parallel}}$ is the parallel component of the electron's momentum in the crystal in the extended zone scheme, i.e. to obtain the momentum in the first Brillouin zone, the respective reciprocal lattice vector G needs to be subtracted [73]. Furthermore, equation 4 neglects the momentum of the incident photon, which is a good approximation for the UV regime but becomes questionable throughout the soft X-ray range [74, 161]. However, I will continue to use this approximation, as it simplifies the fundamental explanation of how ARPES can be used to determine the electronic band structure. The perpendicular component of the photoelectron momentum is not conserved when the photoelectron escapes the solid due to the presence of the surface potential [73, 75, 76, 146]. It can be recovered assuming that the final state dispersion of the electron can be approximated as that of a free-electron, offset by the inner potential V_0 , which can be treated as a phenomenological parameter [74]. This approximation fails if low-energy photon sources are used [74] or if the unoccupied electron bands are of complicated (i.e. not parabolic) shape [162, 163]. For simpler cases, it leads to the following relation for the perpendicular component of the electron's momentum in the crystal:

$$\hbar \vec{k_{\perp}} = \sqrt{2m_e \left(E_{\rm kin} \cdot \cos^2\left(\vartheta\right) + V_0 \right)} \tag{5}$$

The fact that PES measures electrons has several implications that differentiate this technique from X-ray spectroscopies which measure photons, like XAS measured in transmission or fluorescence yield modes or RIXS. Because electrons have a charge, their interaction with matter is much stronger in comparison to photons and they are very sensitive to electric and magnetic fields. Because of the strong interaction with matter in general, the IMFP (the average distance an electron can travel in a solid until it collides with another electron) is very short (see Figure 2.9). In the soft X-ray range, typical values of the IMFP are around 1 nm [157, 164]. This value is, within a certain accuracy, only dependent on the electron kinetic energy, and not the composition of the solid itself. Therefore, photoelectron spectroscopy in the soft X-ray range probes the surface and the first few layers of a solid. In contrast, soft X-rays have a higher attenuation length on the order of 100 nm [70], causing most electron excitations to occur in deeper regions of the sample where electrons can



Figure 2.9: Universal curve of inelastic mean free path (IMFP) of electrons in solids. In the soft X-ray range (purple, 300 eV to 2000 eV), the IMFP amounts to about 1 nm to 2 nm. Data from [76, 157].

not escape without secondary collisions, which cause them to lose kinetic energy. Thus, at kinetic energies below every peak (primary electrons) in an XPS spectrum, the background increases due to an increased number in secondary electrons with a broad distribution of lower kinetic energies [69, 146] (see also the measured XPS spectrum of silver shown in Figure 2.8).

2.5.1 Instrumentation for Photoelectron Spectroscopy

The fact that electrons have a charge also has drastic consequences on the instrumentation which is used to perform photoelectron spectroscopy experiments. Usually, photoelectron spectrometers are operated in UHV with pressures of at least 10^{-10} mbar down to 10^{-11} mbar. Furthermore, electrostatic lens systems can be used to easily and accurately manipulate electrons, making very high energy resolutions below 1 meV possible. Most spectrometers can switch between a real space mode to image the spatial distribution of photoelectrons and an angular mode to record the emission angles of electrons, which is used to determine the band structure in ARPES measurements. Below, the three most commonly used spectrometer types will be described following the description found in [74], as they are all relevant to the experiment described in Paper V [5] (section 4.2) and the future development of the method presented therein. All of the electron spectrometer types discussed below have the possibility to switch between a real space mode to image the spatial distribution of photoelectrons and an angular mode to record the emission angles of electrons, which is used to determine the band structure in ARPES measurements.

The hemispherical analyser is the most widely used instrument for photoelectron spectroscopy [74, 165]. It is versatile regarding energy ranges, as it can detect electron kinetic energies ranging from a few eV to several keV, and source types, as both pulsed and continuous sources can be used. The hemispherical analyser consists of an input lens column which images the angular distribution of the electrons onto an entrance slit to the hemisphere and the hemisphere itself. A potential is applied between the inner and outer part of the hemisphere which disperses electrons along
the radial direction of the analyser: electrons with higher/lower energy are guided on a half-circle with a larger/smaller radius, respectively. On a two-dimensional detector (e.g. a multi-channel plate (MCP)) the non-radial dimension can be used to record one-dimensional information on the electron emission angle (angular mode) or position (imaging mode). To map the respective information in the second lateral dimension of the sample, either the sample or the entire spectrometer need to be rotated, or a scan of deflection electrodes in modern analysers can be used [166]. Hemispheres can achieve an energy resolution down to 1 meV [73, 74, 167–171], with records even below 100 μ eV [172, 173], an angular resolution down to approximately 0.1° and a spatial resolution that depends on the illuminated spot size, which can be below 1 μ m [74]. The angular acceptance angle is typically around ±15°.

In a time of flight (ToF) spectrometer, the kinetic energy of the photoelectron is calculated from the flight time after excitation from the sample by photons. The 40bunch mode of PETRA III with a repetition rate of 5 MHz is ideally suited for such a spectrometer [174]. Since the kinetic energy is encoded in the flight time, both spatial axes of the two-dimensional detector can be used to record the emission angle or position of the photoelectrons, thereby increasing the throughput in comparison to the hemisphere, where energy is recorded on one axis and angular or spatial information on the second. The count rate can be further increased by using a momentum microscope (MM): This relatively new instrumental development [175, 176], uses a high extraction voltage applied to the front lens to collect the entire half-sphere of electrons which are emitted by the sample. When an MM is used in combination with a ToF spectrometer, no slits are needed, which leads to a further increase in transmission in comparison to a hemisphere which uses apertures and collects photoelectrons from a much smaller solid angle.

Photoemission and ARPES have contributed substantially to the field of quantum materials in general [74–76] and e.g. high-temperature superconducting cuprates in particular [45, 73]. Already in the 1990s, high-resolution ARPES studies allowed to resolve the superconducting gap, mapping \vec{k} -dependent effects and investigate the symmetry of the superconducting gap [45].

2.6 Resonant X-ray Diffraction (RXD)

The short wavelength of X-rays, which is approximately equal to interatomic distances in a solid for hard X-rays and on the order of a few unit cells for soft X-rays, allows using them to measure the detailed lattice structure of crystalline solids. When X-rays are incident on a solid, the electrons of each of the regularly arranged atoms emit a spherical wave that interacts with the other emitted waves, leading to interference. Since the density of atoms in a solid is so high (on the order of 10^{23} atoms cm⁻³), diffraction into any direction which does not precisely fulfil the condition of constructive interference is cancelled out and only at the exact angle of constructive interference, singular Bragg diffraction peaks can be observed. This is also known as Bragg's law [177]:

$$n\lambda = 2d\sin\left(\theta\right) \tag{6}$$

Here, the positive integer number n is the index of the constructively diffracted order, λ the wavelength of the X-rays, d the spacing of the lattice planes of the solid and θ the incidence angle with respect to the diffracting lattice planes, see also Figure 2.10. If the number of atoms is limited, e.g. in nanoparticles or thin-films, the width of diffraction peaks increases because intensities at interference conditions close to the perfectly constructive case are not entirely cancelled out any more.



Figure 2.10: Diffraction from lattice planes with a spacing of d according to Bragg's law. Constructive interference occurs at precisely the angle θ at which the path length difference $2d\sin\theta$ equals an integer multiple of the wavelength of the incident radiation $n\lambda$.

When the energy of the incident X-rays is tuned to be in resonance with an electronic transition of an element in the sample, absorption must be included in the scattering process. This is represented in the atomic scattering factor $f(\vec{Q}, \omega)^4$ [77, 115, 179]:

$$f\left(\vec{Q},\omega\right) = f^{0}\left(\vec{Q}\right) + f'\left(\omega\right) + if''\left(\omega\right) \tag{7}$$

Here, \vec{Q} is the transferred wave vector, $\omega = \frac{2\pi c}{\lambda}$ is the frequency of the incident light and $f^0\left(\vec{Q}\right)$ is the Thomson scattering factor, which is the Fourier transform of the atomic charge distribution. In the elastic Thomson scattering process, all electrons, regardless of their shell, play a role. Therefore, it is strongly dependent on the wave vector transfer \vec{Q} . $f'(\omega)$ and $f''(\omega)$ are the real and imaginary parts of the dispersion corrections to f^0 . Furthermore, f' and f'' respectively represent the scattering and absorption terms and as such become particularly important at energies around resonances. f' and f'' are related to each other via the Kramers-Kronig relations and when one of the two is measured, the other one can be inferred [180]. f'' is proportional to the absorption coefficient μ . This shows that the scattering factor, similarly to absorption, has a strong sensitivity to the chemical environment at energies close to resonances. Away from resonances, this is not the case.

The combination of sensitivity to the chemical environment (absorption term, see section 2.4) and sensitivity to order (diffraction term) makes RXD particularly

⁴Sometimes, equation 7 is extended with a magnetic scattering term [77, 178], which is omitted here, since magnetic scattering is not discussed in this thesis.

useful to probe charge, orbital and spin order [77, 179, 180]. The resonance condition additionally provides chemical selectivity and an enhancement of signal levels, as previously discussed for resonant XAS (section 2.4). Typical resonant diffraction signals show a strong peak close to the energy where a resonance is observed in XAS (and at the scattering angle that corresponds to the Miller indices of the reflection). In addition to information on the electronic structure contained in XAS, RXD provides information on electronic order of the measured signal and therefore constitutes a combination of spectroscopy and diffraction.

One example system which was thoroughly study with RXD is magnetite (Fe₃O₄), which is discussed in section 3.3 and publication [4] of this thesis. In magnetite, the energy of the $(00\frac{1}{2})^5$ superstructure peak coincides exactly with the energy of the Fe²⁺ absorption peak, indicating that there is an orbital order to the t_{2g} Fe²⁺ electrons with a periodicity twice that of the high-temperature crystallographic unit cell and the (001) diffraction signal has two peaks at both Fe *B*-site positions due to the charge ordering of Fe²⁺ and Fe³⁺ ions [106]. Thus, resonant diffraction has proven to be invaluable for the investigation of evolution of charge and orbital order during the IMT in magnetite both in the static [105, 106, 181–183] and time-resolved domain [4, 140, 141, 184].

2.7 Resonant Inelastic X-ray Scattering (RIXS)

RIXS is a photon-in photon-out process where the energy of the incident photons is tuned to a core-resonance of the sample. As is also the case for XAS and RXD, this provides element selectivity and enhances the cross section, enabling the study of charge, spin, orbit and lattice degrees of freedom [42, 62, 80]. Working at absorption edges furthermore leads to a better energy resolution, since a well-defined final state is created (as opposed to non-resonant ionization in XES). The RIXS process can be described as a two-step process, combining XAS and XES [62]: In the first step (absorption), an incident X-ray photon with energy $\hbar\omega_i$, momentum $\hbar \vec{k_i}$ and polarization $\vec{\epsilon_i}$ promotes an electron from a core level to an unoccupied state (purple in the RIXS panel in Figure 2.6). The resulting intermediate core-excited state is highly energetic and has a short lifetime on the order of a few femtoseconds [62]. In the second step (emission), this intermediate state decays when a valence electron refills the core hole (blue in the RIXS panel in Figure 2.6) resulting in the emission of a photon with energy $\hbar\omega_o$, momentum $\hbar\vec{k_o}$ and polarization $\vec{\epsilon_o}$. Since RIXS is an inelastic process (as opposed to RXD), the final state is also an excited state with an energy that is usually higher than that of the ground state, but it can also be lower in exceptional cases [185, 186]. The energy and momentum of the final state excitation are respectively:

$$\hbar\omega_f = \hbar \left(\omega_i - \omega_o\right)$$
 and $\hbar \vec{q} = \hbar \left(\vec{k_i} - \vec{k_o}\right)$ (8)

This shows that **RIXS** is both a spectroscopic (change of energy) and a scattering (change of momentum) method. This combination of both properties is similar

⁵If such a superstructure reflection is studied, the RXD is in principle background free, making the method intrinsically very sensitive [69].



Figure 2.11: State diagram of the RIXS process. The total energy of the ground state is defined to be 0 eV. The incident photon (purple) raises the total energy by the photon energy and excites the transition to the intermediate core-excited states. These decay within the short (femtosecond) scattering time, resulting in the emission of a photon (blue) and the creation of valence-excited final states which can include many-particle states like phonons, magnons, etc. (coloured).

to RXD, as described in section 2.6. The differences are the inelastic nature and the resulting final state excitation in RIXS. The final state excitation can occur in the form of different phenomena: Above energies of approximately 1 eV, electronic excitations, like dd- or charge transfer excitations, may occur which, in simple cases, can be explained in the single-electron picture (RIXS panel in Figure 2.6). Collective excitations, like phonons or magnons occur at energies below 1 eV. Because they are collective processes, only the total energy picture, or state diagram, can describe these excitations. In this picture (see Figure 2.11), the ground state energy of the system is defined to be 0 eV. The incident photon raises the energy of the system, promoting it from the ground state to the highly energetic, core-excited, intermediate state. After the scattering time τ_{RIXS} , the intermediate state decays to a final state. As opposed to XAS, where the final state is the short-lived coreexcited state, resulting in fundamentally broad spectral features, the natural line broadening in RIXS is that of the long-lived final state, allowing for narrow lines to be measured [62, 187]. The properties of the excitations probed by RIXS, like their energy, intensity and momentum transfer strongly depend on the investigated system. In Figure 2.11, RXD would be the process where the system returns from the intermediate state back to the ground state.

The cross section σ of the RIXS process is the intensity which is scattered into a differentially small angular volume $\partial\Omega$ with a differentially small energy distribution $\partial\omega$. It is given by the relevant part of the Kramers-Heisenberg equation [42, 62, 79, 80, 188]:

$$\frac{\partial^2 \sigma(\omega_i, \omega_o)}{\partial \Omega \partial \omega} \propto \sum_f \left| \sum_n \frac{\langle f | \mathcal{D}_{\omega_o, \vec{k_o}, \vec{e_o}}^{\dagger} | n \rangle \langle n | \mathcal{D}_{\omega_i, \vec{k_i}, \vec{e_i}} | g \rangle}{E_g - E_n + \hbar \omega_i + i \Gamma_n / 2} \right|^2 \times \delta \left(E_g + \hbar \omega_i - E_f - \hbar \omega_o \right)$$
(9)

- $|g\rangle$ ground state
- $|n\rangle$ intermediate state
- $|f\rangle$ final state

 $\mathcal{D}_{\omega_o,\vec{k_o},\vec{\epsilon_o}}^\dagger$ emission operator for transition from $|n\rangle$ to $|f\rangle$

 $\mathcal{D}_{\omega_i,\vec{k}_i,\vec{\epsilon_i}}$ absorption operator for transition from $|g\rangle$ to $|n\rangle$

- E_q energy of the ground state
- E_n energy of the intermediate state
- E_f energy of the final state
- Γ_n inverse life time of intermediate state

It should be noted, that the elastic RXD process is described by the same formalism, only that the final state corresponds to the ground state [77]. In the Kramers-Heisenberg equation 9, the Dirac-Delta distribution $\delta (E_g + \hbar \omega_i - E_f - \hbar \omega_o)$ warrants energy conservation. The absorption and emission operators $\mathcal{D}_{\omega_i,\vec{k_i},\vec{\epsilon_i}}$ and $\mathcal{D}_{\omega_o,\vec{k_o},\vec{\epsilon_o}}^{\dagger}$ can be evaluated using the dipole approximation (see section 2), as long as the X-ray wavelength is much longer than the involved atomic orbitals (which is a good approximation the case of soft X-rays). The sum over n is the sum over all intermediate states with energy E_n , and since the summation takes place inside the absolute square, all these intermediate states can interfere. Therefore, RIXS measures the quantum mechanical superposition of all intermediate states distributed in the lattice, making it able to investigate collective, momentum-dependent excitations [42].

But how can one assign a peak in the RIXS spectrum to a particular type of excitation? Here, several considerations can help to identify an observed excitation:

First of all, its parameters like the energy loss and momentum dispersion help to classify excitations. Furthermore, the polarization dependence of incident and scattered X-rays can help with the identification in certain cases [42, 189, 190]. For example, the magnetic nature of a magnon excitation around around 100 meV can be distinguished from a phonon mode if a polarization dependence of the emission can be observed [191], since the spin-flip, which occurs during the magnon excitation process, changes the polarization of the photon. Nevertheless, the identification of excitations is not always straight forward. Some excitations can only be seen when certain transitions are involved in the RIXS process. For example, an intermediate state with a 2p core hole with strong spin-orbit coupling facilitates an exchange of angular momentum and thus spin-flip excitations whereas single spin-flips are forbidden with a 1s core hole intermediate state [42]. Because of high energies of X-rays (in comparison to energies used in Raman spectroscopy), higher-energy excitations which have not been seen by any other method, like orbitons [106] can be observed. Also exotic states can be formed during the RIXS process due to the strong distortion of the system, as for example triple, quadruple and quintuple spin flips [192,193]. The opportunity to use RIXS to observe and identify all these different phenomena in solids in combination with the element and orbital sensitivity provided by X-rays make RIXS ideally suited to characterize and disentangle the wealth of excitations and phases in quantum materials.

2.7.1 Comparison to Other Methods

The excitations that can be probed by RIXS can also be investigated with several other methods which are described and compared in the following.

Inelastic X-ray scattering (IXS) is the non-resonant analogue of RIXS. Since IXS operates away from resonances, X-rays scatter from all electrons in the probed material, most of which are tightly bound to the nuclei. Therefore, it is most commonly used to study phonons [194]. Since it operates non-resonantly, IXS beamlines can be optimized for a set of incident energies, allowing to choose the resolution independently of the sample. In the hard X-ray range, where IXS is most often performed, Bragg diffraction from crystals is used for monochromatisation and energy-analysis of scattered radiation. In combination these factors enable energy resolutions even below 1 meV, albeit at the cost of low count rates [194]. Some example studies using IXS to investigate phonons in materials relevant to this thesis, like magnetite and high-temperature super conducting cuprates are references [111, 195]. A general overview on IXS can be found in reference [194].

Electron energy loss spectroscopy (EELS) uses inelastic scattering of electrons. It can measure the collective charge response of a material which comprises (but is not limited to) for example phonons, plasmons or excitons [196]. EELS can be performed in transmission or reflection geometry with respective records in energy resolution better than 1 meV [197] and 5 meV [198]. Transmission EELS requires high acceleration voltages above 30 kV and samples that are not thicker than 100 nm [196]. Achieving a usable momentum resolution at these high electron energies is challenging and comes at the cost of poor spatial resolution (and in turn, a good spatial resolution leads to poor momentum resolution) [196]. Reflection EELS ex-

periments are performed at much lower electron energies in the range of 10 eV to 100 eV, making it easier to achieve high energy and momentum resolution. Thus, EELS has been successfully applied to study low-energy excitations in cuprates [199]. At these energies, electrons do not enter the sample but are reflected above the surface. Therefore, pristine sample surfaces are a strict requirement, necessitating surface preparation techniques, like *in situ* cleaving. Furthermore, EELS can be combined with scanning transmission electron microscopy (STEM). STEM-EELS is the electron analogue of STXM-XAS, which was discussed in the Introduction (see chapter 1), and can achieve spatial resolution even below 1 nm, but poses even more stringent conditions on sample thicknesses (one micrometer is already too thick) due to the limited electron penetration depth [91].

Another inelastic probe using yet another kind of particles as a probe is inelastic neutron scattering (INS). Neutrons are scattered through the interaction of their magnetic moment with the atomic nuclei or with the magnetic moment of unpaired valence electrons [42]. Energy resolutions even below 1 meV can be achieved. This makes INS well-suited for the study of phonons and magnetic excitations. Absolute scattering cross sections can be inferred from INS measurements [200]. Due to comparably large sizes of neutron beams on the order of centimetres and weak interaction of neutrons with matter, much larger sample masses and volumes (on the order of 50 g and 0.1 cm^3 to 1 cm^3) [201] are necessary in comparison to experiments with X-rays at synchrotrons and FELs. INS was used to study magnons in cuprates already before this became possible with RIXS [201].

Raman scattering was predicted more than a century ago [202] and first observed in 1928 [203] by Sir Chandrasekhara Raman, awarding him the Nobel Prize in 1930 [204]. It is a method that is probably much more known than RIXS, which is sometimes actually referred to as (resonant) X-ray Raman scattering [78]. Like in RIXS, energy is transferred from photons to the sample and scattered intensity is measured as a function of energy transferred from photon to sample. As ultraviolet (UV), optical or infrared (IR) light is used, the momentum transferred from the photon to the sample is negligible and phonon and magnon modes are probed at Γ , the centre of the Brillouin zone. Raman scattering can also be performed in resonance. However, owing to the low photon energies, only valence levels are accessible. With RIXS on the other hand, the selectivity of soft X-rays (which was described above) can be used to study excitations originating at a specific site in the material of interest and the significant momentum transfer can be used to map out the dispersion of excitations. In Raman scattering, selection rules determine, which modes can be observed; often phonons are classified e.g. as Raman-active (change of polarisability) or IR-active (change of dipole moment). This can be used for example to observe phase transitions in solids that cause a change of symmetry, leading to modes that appear or disappear [194, 205]. Raman scattering can also be used to investigate magnetic excitations [206, 207], for example to see magnon excitations in high-temperature superconducting cuprates [208, 209]. Raman scattering experiments can be performed with small spot sizes below 1 µm, allowing for the investigation of coexisting phases in quantum materials, as for example shown for Y_{0.63}Ca_{0.37}TiO₃, which is also subject to the study presented in Paper III of this thesis (see section 3.2.3 [3]).

2.7.2 Beamlines and Instrumentation for RIXS

The energy of a RIXS excitation is the difference of the incident and emitted photon energies (often referred to as energy loss). To determine the energy loss the energy of the scattered photon needs to be measured. The instrumentation used to achieve this drastically differs depending on the X-ray spectral region that is used: In the soft X-ray range, usually diffraction off a reflective grating that disperses scattered X-rays across a detector is used and will be discussed in more detail below. On the other hand, RIXS instruments operating in the hard X-ray regime use Bragg crystal optics and are therefore fundamentally different in their opportunities and challenges. In the intermediate energy regime, ranging roughly from approximately 2 keV to 5 keV, in principle both grating and crystal optics are possible, but for example the IRIXS spectrometer at beamline P01 of PETRA III in Hamburg successfully uses a combination of mirrors and crystal optics to achieve an energy resolution down to 35 meV [210, 211]. Further discussing tender and hard X-ray RIXS instruments is beyond the scope of this thesis and further information on these topics may be found elsewhere [80, 210–213]. In the following, this section focuses only on soft X-ray **RIXS** instrumentation.

Because of two factors, RIXS is a very photon-hungry method: First of all, as discussed in the XAS chapter 2.4, the dominating decay channel of a core-excited state in the soft X-ray range is the non-radiative emission of electrons (see Figure 2.7). The likelihood of a radiative decay is only on the order of 0.1% to 1%. Secondly, RIXS photons are emitted isotropically from the sample, but gratings only cover a small fraction of the 4π solid angle: Because X-rays are incident under grazing angles of below 3° on the grating (to obtain a high reflectivity), the effective aperture is only on the order of 3 cm by 0.5 cm. A typical distance to the sample is 30 cm, resulting in a collected solid angle fraction of 10^{-4} . Combining this with the low fluorescence yield and a spectrometer grating efficiency in the range of 10% to 40% (depending on the desired resolution) [83, 85] means that only a fraction of approximately 4×10^{-7} to 10^{-8} of the incident photons are detected. The quantum efficiency of typical detectors like a CCD or CMOS detector is close to 1 [87]. Therefore, typical acquisition times for one RIXS spectrum at a synchrotron radiation source is around half an hour to one hour.

Achieving a reasonable count rate in combination with a high energy resolution is a technological challenge. Therefore, RIXS is a technique which is only feasible at large-scale facilities like synchrotron radiation sources and free-electron lasers. The entire beamline and spectrometer have to be optimized for resolution and flux to make RIXS experiments feasible. A typical high-resolution RIXS beamline features five optical elements (4 mirrors and the monochromator grating) in the beamline upstream of the sample and an extremely small spot on the sample measuring only a few micrometres in the energy-resolving dimension of the spectrometer [83, 85, 86, 214–216]. The spectrometer additionally features up to three optical elements (between zero and two mirrors and the spectrometer grating) downstream of the sample. Typically, no slits are used in the spectrometer, which means that the resolution of the spectrometer critically depends on the spot size of the incident beam on the sample. Moreover, the resolution depends on dispersion of the grating, the surface quality of all optical elements and finally the pixel size of the detector. In order to maximize the reflectivity of the soft X-rays, all optical elements are typically operated at incidence angles below 2° [83, 85, 86, 88], making the footprints of the beam on the optics quite large, even for small beam diameters. To be able to hold up the extreme resolution requirements of ultra-high-resolution **RIXS** experiments, the surface quality of the mirrors and gratings needs to be extremely good across the entire surface, ideally realizing a slope error below 0.1 µrad [85] or a surface roughness of about 0.3 nm [86] bordering on what is technically feasible [85, 217]. The grating line density determines the degree of dispersion, with common values of $1000 \,\mathrm{mm}^{-1}$ to $2000 \,\mathrm{mm^{-1}}$ and up to $5000 \,\mathrm{mm^{-1}}$ [83, 85, 86, 214–216, 218]. These values are practically at the limit of technological possibilities [81, 217, 219]. Realizing all these technological challenges, a combined resolving power $\frac{E}{\Delta E}$ (with the photon energy E and the energy resolution ΔE) of up to 42 000 has been demonstrated experimentally at the SIX beamline at the synchrotron radiation source NSLS-II, which translates to a resolution of 22 meV at a photon energy of 930 eV, corresponding to the copper L_{3} edge [220]. Resolving powers around 30 000, corresponding to approximately 30 meV are achieved routinely [86], just good enough so that investigations of phonons and electron-phonon interactions with RIXS can be conducted [218, 221, 222]. These energy scales correspond approximately to the thermal energy at room temperature $293 \,\mathrm{K} \approx 25 \,\mathrm{meV}$. Current efforts to further improve the resolving power to $70\,000$ at NSLS-II [82, 223] and even to 150000 [86] to resolve e.g. low-energy phonons or the opening of the superconducting gap [224] are ongoing. These resolving powers correspond to energy resolutions on the order of 10 meV which would allow to study low-energy phonons and the superconducting gap in cuprates.

To conclude this section, realizing these ultra-high energy resolutions requires stable optics with an almost perfect surface quality producing no aberrations, detectors with small pixel sizes, gratings with very high line-densities and spectrometer arm lengths of well beyond 10 m. To be able to cover a the majority of reciprocal space, the scattering angle 2θ needs to be adjustable, meaning that the spectrometer arm needs to be able to rotate around the sample chamber. Combining this with the large spectrometer size implies that these RIXS instruments are often build in dedicated buildings [82, 83, 85]. Past and current efforts try to push the resolution to its limit by developing new detectors [225], manipulating optics surfaces almost down to the atomic level [85, 86], increasing the spectrometer size to 15 m [82, 83, 85, 86], producing higher line density gratings [81, 217], and realizing new approaches to increase the dispersion of soft X-ray gratings [219].

2.8 Status Quo and Limitations of Contemporary X-ray Spectroscopy

So far, several soft X-ray spectroscopic techniques which are highly relevant for past, current and future studies of quantum materials have been introduced above. Together, they present a comprehensive toolbox enabling one to select the method that fits best to the material and phenomenon that is subject to a scientific study. However, some limitations persist in the way how contemporary X-ray spectroscopy experiments are performed. Below, two emerging major challenges are described which need to be addressed in order to uphold the success that X-ray spectroscopy has proven for the study of quantum materials.

The first challenge concerns the study of non-homogeneous samples: Typically, the signal which is measured from the illuminated spot on the sample is averaged, meaning that the spatial resolution of the measurement is that of the spot size. However, as previously described, it is not uncommon for quantum materials to exhibit spatial inhomogeneities on the micro- and nanoscale (see section 2.1.2) [54, 112, 226-228]. If the signal is averaged from a focus that is larger than the domain size, one measures the average, weighted by the volume ratio of the illuminated phases. The conceptually simplest approach to adapt existing methods to this challenge is to decrease the spot size as much as possible and scan a small X-ray spot across the sample [104, 112]. This scanning approach has the drawback that measurements are done subsequently making them somewhat susceptible to systematic errors or changing external parameters. Furthermore, the smaller the X-ray focus and step size between measurement positions is, the more rigid are the requirements to stability and motor movement precision. Lastly, a smaller spot leads to an increased flux density on the sample and thus potential sample damage. Specifically for (conventional) RIXS, such a scanning approach is difficult to realize because a full dataset requires many spectra to be measured [62].

The other challenge concerns specifically the continuous improvement of achievable energy resolution in RIXS: As detailed in the previous section (see section 2.7.2 for references and details), the instrumentation used nowadays are approaching the technological limits regarding, for example, the size of the spectrometer arm, the line density of gratings, surface quality of reflective optics and the pixel size of the detectors. And, while there are new concepts for some of these items, the costs for an instrument that utilizes the newest developments will certainly be rather high.

In the following chapters of this thesis, experimental approaches are presented to tackle these challenges: With the RIXS imaging setup (section 3.2), XAS and RIXS experiments can be performed with a spatial resolution of about 2 µm. Furthermore, this approach significantly increases the utilized photon flux by making use of the entire photon bandwidth provided by the beamline monochromator through the fully open exit slit. The flux density on the sample is not increased in comparison to a conventional XAS or RIXS experiment, because the monochromator bandwidth is distributed over a large area on the sample, which is imaged onto a two-dimensional detector. On the other hand, the method of photoelectron spectrometry for the analysis of X-rays (PAX) (see chapter 4) presents a fundamentally different approach in comparison to grating-based RIXS. PAX promises to address the need for increased energy resolution in **RIXS** by utilizing the high energy resolution that can be achieved with electron spectrometers, as described in section 2.5. The energy resolution in PAX does not depend on the spot size, which alleviates concerns about sample damage. Additionally, a range of approximately up to a quarter of the first Brillouin zone can be measured simultaneously without the necessity for moving the sample or spectrometer - meaning that also the spot size and position are guaranteed to remain the same. In the future, a dedicated ultra-high vacuum (UHV) chamber, will allow to complement PAX with ARPES measurements, taken from the same sample spot.

3 Transmission Zone Plates for Soft X-ray Studies of Quantum Materials

This chapter discusses the application of transmission Fresnel zone plates [232, 233], which can be employed either as X-ray imaging optics or - if only an off-axis part of the zone plate is used - as dispersive component in X-ray spectrometers for RIXS, RXD and XES experiments [234]. For the results presented in this thesis, transmission zone plates play a central role, as they were used in four experiments, where both applications for zone plates are combined for multidimensional and multimodal X-ray studies of quantum materials. The experimental approaches are illustrated in Figure 3.1. The first section 3.1 of this chapter gives a general introduction to zone plates, focusing on zone plate properties and parameters. The use of offaxis zone plates specifically for X-ray (imaging) spectroscopy (top in Figure 3.1) is introduced in section 3.2 and detailed in Paper I [1] (section 3.2.1). Paper II [2](section 3.2.2) presents an application of this method to study the insulator-to-metal transition (IMT) in vanadium dioxide thin film microstructures. Furthermore, the applications of zone plates are continued by full-field diffraction imaging (middle in Figure 3.1) described in Paper III [3] (section 3.2.3). Finally, a zone plate was used for time-to-space mapping, a method which maps the pump-probe delay as well as pump laser fluence in time-resolved FEL experiments onto a two-dimensional detector (lower panel in Figure 3.1) as demonstrated in Paper IV [4] (section 3.3). Thus, this chapter describes how zone plates offer unique flexibility to study various properties of quantum materials in several dimension, including the two-dimensional position with (currently) micrometer resolution, incident photon energy, emitted photon energy, time and pump laser fluence with several different X-ray methods like XAS, XES, RXD, RIXS and XRD.

The experiments presented in Papers I-IV [1-4] were performed in the ultrahigh vacuum chamber for multidimensional spectroscopy and inelastic X-ray scattering (MUSIX) [12, 186], with the exception of the full-field diffraction imaging of $Y_{0.63}Ca_{0.37}TiO_3$ (section 3.2.3 [3]), for which the - very similar - endstation ResScatt [235] was used. Both chambers offer great flexibility for soft X-ray studies of quantum materials at synchrotron and FEL facilities with respect to geometry (incident and scattering angles, horizontal or vertical scattering plane), detection schemes (diode, in-vacuum charge-coupled device (CCD), spectrometer or externally attached detector arm), sample environments (currents, magnetic fields) and, in consequence, methods which can be applied (XAS in total or partial EY or FY mode, reflectivity, XES, RXD, XMCD, RIXS) as well as the novel zone plate schemes described below.



Figure 3.1: Multidimensional and multimodal measurement schemes involving off-axis zone plates used in this thesis. RIXS imaging (P04 [229], PETRA III) can be used for measurements of XAS, XES and RIXS with spatial resolution of about 2 µm [1], for example to study the thermally induced insulator-to-metal transition (IMT) in VO₂ microsquares [2]. Full-field diffraction imaging (P04 [229], PETRA III) presents an efficient method to selectively observe the thermal evolution of insulating and metallic domains within a metallic surrounding in Y_{0.63}Ca_{0.37}TiO₃ [3]. For a study of the ultrafast, laser-induced IMT in magnetite (Fe₃O₄) with resonant X-ray diffraction, the time-to-space mapping method (BL2 [65, 230, 231], FLASH1) can be used to map an extended range of both the pump laser fluence and the delay between pump and FEL probe onto the detector [4].

3.1 Introduction to Zone Plates

In general, several types of zone plates exist. They can either be used in transmission or reflection geometry. Transmission zone plates can furthermore be subdivided into absorbing or phase shifting zone plates. The following discusses mostly absorbing transmission zone plates, since this type of zone plates were used in the experiments presented in Papers I-IV. A thorough introduction to the formalism of zone plates is given in [116], whereas [236] presents an instructive overview. A transmission zone plate consists of thousands of concentric zones with an increasing radius and decreasing zone width towards the outer edge. The zones are alternately opaque and transmissive, as schematically shown in Figure 3.2a. A monochromatic plane wave of wavelength λ is focused at the focal distance f from the zone plate if diffraction from every neighbouring transmissive zone (i.e. from every second zone) interferes constructively. Therefore, the path length difference Δs of neighbouring opposing zones (opaque-transmissive) has to be $\lambda/2$ and between next-neighbouring zones of the same kind has to be λ :

$$\Delta s_n = \frac{n\lambda}{2} \tag{10}$$

If we consider plane wave illumination, and l_n is the distance from the n^{th} zone's outer edge to the focus at f (see Figure 3.2), this means that:

$$l_{n+1} = l_n + \frac{\lambda}{2}$$
 and $l_{n+2} = l_n + \lambda$ (11)

Here, n is an integer zone index between 1 and the maximum number of zones N of the zone plate. From the red circle segment in Figure 3.2b, one can see that the path length difference Δs_n between f and l_n is given by:

$$\Delta s_n = l_n - f \tag{12}$$

Comparing equations 10 and 12 and applying Pythagorean theorem leads to

$$l_n - f = \frac{n\lambda}{2} = \sqrt{r_n^2 + f^2} - f$$
(13)

which can be solved for r_n :

$$r_n^2 = n\lambda \left(f + \frac{n\lambda}{4} \right) \tag{14}$$

Equation 14 is the 'recipe' how the radius r_n has to increase with n for a zone plate to focus a plane wave of wavelength λ at the distance f. The term $\frac{n\lambda}{4}$ can be neglected if it is much smaller than f (typically on the order of cm or mm), which is a good approximation for soft X-rays (wavelength of about 1 nm to 5 nm). Thus, equation 14 simplifies to the zone plate equation:

$$r_n \approx \sqrt{n\lambda f}$$
 (15)

This shows, that the zone radius increases with the square root of the zone index \sqrt{n} . Furthermore, equation 15 shows an important property of zone plates if



Figure 3.2: Transmission zone plate properties and focusing. Panel a: A full zone plate with an off-axis part highlighted. Panel b: Side view of the first few inner zones of a zone plate focusing a monochromatic plane wave of wavelength λ . A focus is created at the focal length f if the path length difference Δs_n between neighbouring transmissive zones corresponds to λ (see text). Some parameters are defined for the example of the first zone but can be generalized to any zone n: the radius of a zone r_n , the distance of a zone's edge to the focus l_n , the path length difference between a zones n and n-1 (red line), and the half opening angle θ_n . For simplicity, only the first convergent (+1st) diffraction order is shown.

non-monochromatic light is used: The focal length of the zone plate is inversely proportional to the wavelength and proportional to the photon energy, i.e. zone plates are chromatic.

Another important design factor for zone plates is the outermost zone width Δr . As one can show, Δr is proportional to the theoretical limit for the spatial resolution Δx of the zone plate according to the Rayleigh criterion¹ [116]:

$$\Delta x = 1.22\Delta r \tag{16}$$

Thus, the resolution which can theoretically be achieved with a zone plate is limited by how small the smallest structures are that can be fabricated. In practice, the resolution can be diminished due to imaging aberrations or fabrication imperfections. The material used for zone plates varies depending on the desired photon energy and absorption/phase shift properties at that energy. Materials used for zone plates are for example gold [116, 237, 238], nickel [237, 239], iridium [240] or germanium [116]. For the studies that are part of this thesis, zones consisting of SiO₂ on a silicon nitride membrane were used [234]: A thin silicon nitride membrane is

¹According to the Rayleigh criterion, two mutually incoherent, quasi-monochromatic point sources can be discerned from each other if their respective Airy patterns, formed by an ideal zone plate in the imaging plane, are so close to each other that the first null of one just coincides with the maximum of the other. This results in smallest resolved separation of $\Delta r_{\text{null}} = 0.61\lambda/\text{NA}$, where $\text{NA} = \sin \theta$ is the numerical aperture.

coated with a layer of hydrogen silsesquioxane (HSQ), which is then exposed to the 100 kV electron beam of an electron beam writing machine to write the structures of the zone plate. Being exposed to these high-energy electrons, HSQ becomes similar to SiO₂. A developer then removes the non-exposed parts of the HSQ film. The limits of the smallest structures which can be fabricated using this method is well below 50 nm and focus sizes below 10 nm have been achieved in zone plate-based soft X-ray microscopes (see e.g. [92–94]). Another important factor for the achievable resolution is the magnification. One can show [116] that the magnification of a zone plate is defined as the ratio of the object distance q from source point to zone plate to the image distance p from zone plate to detector; i.e. analogous to the magnification of a refractive lens for optical light.

So far, only the positive (focused) first diffraction order was discussed. Similarly to a diffraction grating, other diffraction orders also need to be considered [116]. For a transmission zone plate, the negative diffraction orders are divergent (with virtual foci upstream of the zone plate), and positive convergent diffraction orders have a focal length which is reduced by $f_m = f/m$, where m is the index of the diffraction order. Electric fields which would contribute to even diffraction orders cancel out for the types of zone plates discussed here [116]. The zeroth order is the undiffracted part of the incident beam which is transmitted in forward direction. The intensity contribution diffracted into other orders affects the first order transmission of the zone plate: In a basic zone plate with opaque and transmissive zones designed according to equation 15, 50% of the incident intensity is absorbed in opaque zones and 50% is transmitted. Thereof, approximately 25% are transmitted into the zeroth order, about 10% into each the plus-first and minus-first orders, and around 1% into both third orders. The first order diffraction efficiency can be increased by using phase shifting zones instead of opaque zones [239, 241] or by using nonrectangular zone profiles [242]. With these methods, first order efficiencies of 15% to 20% in the soft X-ray range can be achieved. Phase shifting zone plates are another kind of zone plates which introduce a phase shift of π to the light diffracted from every other zone, making it add constructively with the open zones [116]. Achieving this exact phase shift necessitates a specifically selected combination of material, thickness and operating wavelength. Some example parameter sets are shown in reference [237].

3.2 Soft X-ray Spectroscopy and Scattering with Micrometre Resolution

After introducing the general composition and properties of Fresnel zone plates, the following section specifically describes how the imaging properties of zone plates can be combined with measurements of RIXS (section 3.2.1), XAS (section 3.2.2) and diffraction 3.2.3. The application to time-resolved RXD is described in section 3.3. For all these experiments, off-axis zone plates were used, as already shown in Figure 3.2 and detailed below. One general advantage of off-axis zone plates is that the positive first diffraction order is directed away from the zeroth order beam, so that only the first order reaches the detector. Thus, an order-sorting aperture can be

omitted.

3.2.1 Soft X-ray Spectromicroscopy

The chromatic focusing of zone plates according to equation 15, which was discussed in the previous section 3.1, may present a challenge to experiments because the incident beam needs to be highly monochromatic in order to avoid an enlarged focus. Figure 3.3a illustrates this situation: Two colours (representing two photon energies) are focused at two distinct focal lengths (A and C). At the focus position of one colour, the other is defocused. Because of this chromatic focusing behaviour, the off-axis part of a zone plate (as shown in Figure 3.2a) can also be used to disperse photon energies and therefore, off-axis zone plates can replace reflective gratings as dispersive element in spectrometers [234, 243], as already shown in Figure 3.1 at the beginning of this chapter. Figure 3.3b shows how different colours are separated on a two-dimensional detector when an off-axis zone plate is used. By varying the position of the detector along the optical axis, the photon energy with the best focus can be selected.



Figure 3.3: Chromaticity of zone plates. Point-to-point imaging of a source containing two colours by a full zone plate (panel a) and an off-axis zone plate (panel b). The longer wavelength (red) is focused at a shorter focal distance (see equation 15). Placing a detector at different distances along the optical axis (i.e. A, B, C) allows choosing the focused wavelength, but no matter where the detector is placed, the different colours always overlap on the detector image. If only an off-axis part of the zone plate is illuminated (panel b), the colours are dispersed across the detector (A', B', C').

In addition to the capability to serve as dispersive element, off-axis zone plates retain the imaging properties of the full zone plate and thus present (in a single object) a possibility how X-ray spectroscopy can be combined with spatial imaging (upper panel in Figure 3.1). Also imaging diffraction experiments can be performed with zone plates, by placing the optic at the position corresponding to the lattice reflection indices of interest (which was done in the full-field diffraction imaging experiment shown in the middle panel in Figure 3.1). By using an off-axis zone plate instead of the full zone plate, the image (usually first order) is separated from the part of the incident beam that is transmitted into the zeroth order, enabling a low-background signal detection without the need for an order-sorting aperture.

With off-axis zone plates, the information density acquired with RIXS can be increased using an approach sometimes referred to as two-dimensional RIXS (2D-RIXS) [81, 86, 244]. In a typical RIXS experiment, a two-dimensional detector is used to measure the RIXS spectrum along the dispersive direction of the spectrometer. The RIXS spectrum is spread out across the second, non-dispersive direction of the detector screen, but no actual information about the sample is contained in this dimension. During the data analysis, this dimension is usually integrated. If an off-axis zone plate is used as analyser instead of a grating, the RIXS signal in the non-dispersive dimension is focused to a line on the detector [1, 234, 243]. In this case, the RIXS spectrum from a monochromatic focus on the sample presents one-dimensional data and the non-dispersive dimension is available to increase the information density recorded in a single detector acquisition. This can be done by focusing the incident X-rays to a line on the sample which extends along the non-dispersive dimension. If this line is of monochromatic composition, a spectrum is measured for every spot along the line focus, allowing for simultaneous one-dimensional spatially resolved RIXS measurements. If instead the incident photon energy varies along the line focus (which can be achieved by simply opening the exit slit of a monochromator beamline), a RIXS map can be measured in a single acquisition. Because the exit slits are otherwise closed in a typical RIXS experiment, the additional photons are obtained for free and the **RIXS** map is measured in the same time which would otherwise be needed to measure a single spectrum.

The idea to acquire RIXS spectra (energies $h\nu_{out}$) simultaneously for a range of incident energies ($h\nu_{in}$) has been formulated for spectrometers using reflective optics, dubbed $h\nu^2$ -spectroscopy [244]. However, a single grazing incidence mirror produces an image plane at an angle close to the grazing angle, implying that aberrationfree imaging with a single mirror is only possible close to the optical axis [234, 245]. The solution is using two mirrors, in a Wolter-type I configuration [246]. In combination with the grating, and potentially an additional pre-mirror, this results in an arrangement of four grazing incidence optical elements in the spectrometer which are required to be able to image a line focus of about a one millimetre length onto the detector [247]. This leads to high levels of cost and complexity for such a spectrometer: since all its elements need to operate at grazing angles they are very sensitive to misalignment, instabilities and surface slope errors [86]. Several instruments using the grazing incidence approach for 2D-RIXS are currently under construction [86, 216, 245, 247].

In comparison to the 2D-RIXS approach, an imaging spectrometer setup using an off-axis zone plate is insensitive to small misalignments [234]. Such a setup is presented in Paper I (see top panel in Figure 3.1), demonstrating a spatial resolution of $1.8 \,\mu\text{m}$, which was achieved by realizing a magnification factor of 11.5 with a sample-zone plate distance of approximately 15 cm and a zone plate-detector distance of 1.7 m. This spatial resolution was mainly limited by the magnification factor and detector pixel size of 13.5 µm. To increase the magnification, one can either position the detector further away from the zone plate, or bring the zone plate closer to the sample. While the distance to the detector is limited by the available space in the experimental area, in the future, the resolution can be improved by designing a zone plate that can be positioned closer to the sample. The energy resolution that can be achieved with the zone plate setup depends on limiting contributions from the detector, a geometric contribution, a diffraction-limited contribution and the photon energy bandwidth delivered from the beamline [234]. In general, it critically depends on how small the outermost zone Δr is. In reference [234], the energy resolution achieved with an off-axis zone plate was a factor of two worse in comparison to reflective grating analyser used at the same beamline with comparable settings. More details on the comparison to a grating-based setup and the energy resolution can be found in [234].

In the following paper², entitled "Soft x-ray imaging spectroscopy with micrometer resolution", we present the RIXS imaging setup and demonstrate a spatial resolution of $2 \,\mu\text{m}$.

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Soft x-ray imaging spectroscopy with micrometer resolution

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Soft x-ray spectroscopy is invaluable for gaining insight into quantum materials. However, it is typically conducted in a spatially averaging way, making it blind to inhomogeneity in samples. Here, we demonstrate how we couple imaging to x-ray absorption spectroscopy and resonant inelastic x-ray scattering. Accordingly, we use a 2D detector and an off-axis Fresnel zone plate that images the sample in one spatial dimension and provides spectroscopic information in the other dimension. With our setup, we envision to enable a more detailed understanding of how the behavior of microscopic domains determines the functionality of quantum materials.

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1. INTRODUCTION

Functionality in quantum materials is driven by a delicate balance of contributions from different interacting degrees of freedom: the electronic subsystem with different spin arrangements, orbital occupations or charge distributions, and the lattice contributions [1,2]. This interplay can yield a variety of energetically close-lying states. Therefore, it is relatively easy to switch between different states by tuning external parameters such as temperature, pressure, or chemical composition. Together with chemical inhomogeneity, pinning centers, crystal defects, or even spontaneously forming phase separation, such an energetic environment is prone to form microscopic domains with distinct electronic properties. The macroscopic functionality is a result of the detailed combination of different local situations together with their spatial arrangement [3].

Some recent work highlights the importance of studying electronic properties on microscopic length scales to understand the macroscopic properties. Important spatially varying textures have been observed in various quantum materials, such as in the high- T_c superconductor HgBa₂CuO_{4+y} [4], in the titanate compound Y_{0.63}Ca_{0.37}TiO₃ [5], and also in vanadium dioxide (VO₂), the well-known material with an insulator–metal transition near room temperature [6–9].

Modern soft x-ray spectroscopy methods, such as x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS), provide a highly selective way to study fundamental properties of materials [10,11]. However, these methods often do not resolve microscopic domains in solids. If these methods are applied to inhomogeneous samples, an average response from all electronic domains under x-ray illumination is measured. Therefore, it is highly desirable to achieve microscopic spatial resolutions with XAS and RIXS. Typically, during RIXS measurements, x-ray energies emitted from the sample are recorded for a set of incident energies, which is commonly referred to as "RIXS maps." Such a measurement can be parallelized if the set of excitation energies produces spectra at different positions on a two-dimensional detector. The most natural realization of this concept is the combination of spatially dispersed radiation on the sample with an imaging spectrometer, allowing to record entire RIXS maps of homogeneous samples in one exposure. Such a setup additionally allows studying inhomogeneous samples with high spatial resolution. Several approaches in the soft [12-15] and hard [16] x-ray regime have been conceptualized. Most proposed realizations combine multiple mirrors and a grating.

In this work, we present a RIXS-imaging setup that allows measuring XAS in partial fluorescence yield and RIXS with a

spatial resolution down to 1.8 µm over a field of view of nearly 1 mm. Spectral and spatial information is simultaneously recorded and mapped onto the two dimensions of a CCD detector using the chromatic imaging properties of a transmission off-axis analyzer zone plate (AZP). The zone plate is the only optical element between the sample and detector. Its alignment is straightforward [17], limited to the one-dimensional positioning of the AZP along the optical axis to within several hundred micrometers. The RIXS-imaging concept is based on previous work presenting considerations concerning the energy resolution of an AZP-based spectrometer [18] as well as first spatially resolved measurements [17]. Here, we present an advanced setup that uses a second transmission zone plate upstream of the sample and a substantially larger sample magnification to achieve a peak spatial resolution of 1.8 µm, and we explain how we are able to record spectral and spatial resolution within a single measurement. This achievement paves the way to a more detailed understanding of the behavior of quantum materials on the microscale [19].

For the use of the RIXS-imaging setup, it is essential to understand the focal properties of zone plates and the behavior of spatial and energy resolution for energies that are in and out of focus on the detector. The focal length of a zone plate is approximately proportional to the diffracted photon energy (see Supplement 1). To estimate how wide the sufficiently resolved energy range in an AZP experiment is, one has to define the accepted limits of spatial and energetic resolution for energies ΔE that deviate from the energy at the optimal focus. This in turn determines the bandwidth $2\Delta E$ of emitted radiation that can effectively be recorded at the same time. Setting the AZP to focus the photon energy E_0 onto the detector results in a larger and defocused spot for an energy $E' = E_0 + \Delta E$. The spatial resolution on the sample Δx_{Sample} and the energy resolution dE for a small deviation ΔE from the focus energy E_0 are given by

$$\Delta x_{\text{Sample}} = w \frac{\Delta E}{E_0} \cdot \frac{M+1}{M},\tag{1}$$

$$dE = \frac{w}{\bar{r}} \cdot \Delta E. \tag{2}$$

Here, $w = r_{out} - r_{in}$ is the (radial) width of the off-axis zone plate, *M* is the magnification, and $\bar{r} = (r_{out} + r_{in})/2$ is the mean AZP radius. The derivation is sketched in Supplement 1, which expands on [18]. For example, when the used AZP is set to focus $E_0 = 530 \text{ eV}$, for an energy offset of $\Delta E = 1 \text{ eV}$, the spatial resolution degrades to 6.2 µm, and the energy resolution to 0.94 eV (see also Table S1). Both values increase mostly linearly for larger energy offsets. This chromatic defocusing contribution to spatial and energy resolution adds to contributions from detector, x-ray beam, the quality and alignment of the zone plates, and, ultimately, the diffraction limit [18] and becomes dominant for energies away from the center energy. Close to the focus, we measure a spatial resolution of 1.8 µm (see below), and estimate an energy resolution to 0.35 eV. Applying the formulas in [18] yields a similar result.

2. EXPERIMENT

The measurements are performed using the ultra-high vacuum endstation MUSIX [20] at the soft x-ray beamline P04 [21] at PETRA III, DESY in Hamburg. In our RIXS-imaging setup, the entire dispersed beam provided by the beamline is used to form a vertical line focus on the sample. Along this line, the sample



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Fig. 1. (A) Schematic experimental setup and (B), (C) determination of spatial resolution. (A) A linear illumination zone plate and beamline components are used to create a sub-micrometer-wide and ~970 μ m long x-ray line focus on the sample. An off-axis Fresnel zone plate between sample and detector images the sample in direction of the focus line and disperses emitted x-rays in perpendicular direction. (B) Microstructured VO_x on Si₃N₄ Siemens star sample for spatial resolution characterization as seen by an optical microscope. (C) The line focus at the highlighted position in (D) excites oxygen *K*-edge fluorescence, yielding the shown image (background subtracted). (D) The vertical focus line is scanned across the Siemens star in horizontal direction, and the signal is integrated along the horizontal direction between the white lines indicated at top and bottom in (C). Scale bars are 50 μ m.

is imaged and magnified onto the detector. The perpendicular direction on the detector is used to spectrally analyze x-ray emission from the sample. The RIXS-imaging setup can be applied in various modes that require a measurement strategy different from more conventional setups: (1) for heterogeneous samples and rather featureless spectra (e.g., fluorescence), the focus line and an orthogonal unidirectional scan can be used to map the sample structure; (2) for homogeneous samples, a so-called RIXS map (inelastic scattering spectra for a set of excitation energies) can be recorded in-parallel without any scan; (3) for heterogeneous samples with complex spectra, by scanning the sample surface as well as the excitation energy, high-dimensional information can be recorded, as will be described in more detail below. For both spatial mapping and energy analysis, the horizontal width of the line focus is required to be very small for optimal resolution. For this purpose, we refocus the incident x-rays horizontally with a linear transmission illumination zone plate (IZP) serving as cylindrical lens (Fig. 1A).

The monochromator of beamline P04 disperses x-rays vertically. We use a 400 line \cdot mm⁻¹ grating with a fix-focus constant c_{ff} of 1.6 [21], yielding a dispersion of 1.25 eV \cdot mm⁻¹ in the exit slit plane at a photon energy of 530 eV. A bandwidth of 3.6 eV is transported onto the sample, if we open the exit slits as far as possible (2.9 mm). Importantly, this broad bandwidth does not affect the RIXS energy resolution in our setup, but provides a range of excitation energies that can be detected in-parallel and permits utilizing a substantially higher fraction of the produced photon flux in comparison to working with a narrow bandwidth. The refocusing mirrors of beamline P04, located between the exit slit and the IZP (for clarity, not shown in Fig. 1), demagnify the exit

slit by a factor of three in the vertical direction. On the sample, the x-ray line focus thus measures approximately 970 µm vertically.

Horizontally, the refocusing mirrors are set to quasi-collimate the beam. The IZP has an aperture of $3.8 \text{ mm} \times 1.9 \text{ mm}$ (v × h) and a focal length of 149.3 mm at an x-ray energy of 530 eV (see also Supplement 1). The first-order diffraction efficiency is around 5%–10%. Nanopositioning stages (SmarAct GmbH) allow for motion of the IZP in all three spatial dimensions, as well as tilt around a horizontal axis (perpendicular to the incident beam). This tilt is used as compensation for the chromatic behavior of the IZP: when changing the central incident photon energy, the IZP position along the beam is adapted to keep the focus on the sample. Two motorized baffles between IZP and sample serve as order sorting apertures.

In the spectrometer, the use of the transmission off-axis Fresnel zone plate allows to resolve spatial and spectral information from the sample at the same time [17,22]. The AZP has a size and aperture of 3 mm \times 3 mm. The outer radius and outermost zone width are 4.7 mm and 35 nm, respectively. At a photon energy of 530 eV, the focal length is 140.7 mm. The first-order diffraction efficiency is approximately 10%-15%. The AZP is oriented to disperse x-rays in the horizontal and image in the vertical (direction of line focus). Both IZP and AZP are supported by a 100 nm thin silicon nitride membrane (see Supplement 1). This can cause apparent spectral variations for measurements in close proximity of the nitrogen and silicon absorption edges. For such measurements, pure silicon and carbon-based membranes should be used. Like the IZP, the AZP is also mounted on 3D nanopositioning stages for alignment and focus optimization. To focus different parts of the emission spectrum onto the detector, the AZP is moved along the sample-detector axis.

The detector is a direct detection CCD camera (Andor iKon-M) with a pixel size of $(13 \,\mu\text{m})^2$. The AZP is positioned at an object distance of 0.15 m and an image distance of 1.725 m, resulting in a magnification of 11.5. This enables us to achieve micrometer resolution. The camera is shielded from visible light with a 200 nm thin aluminum filter.

3. RESULTS

We used a Siemens star test structure to determine the overall spatial resolution of the setup. An optical microscopy image of this star is shown in Fig. 1(B). The star has a diameter of 500 μ m and 72 spokes that consist of an oxide of vanadium (VO_x) deposited on silicon nitride (Si₃N₄). During the measurements, the angle of the sample normal in the horizontal scattering plane is 30° w.r.t the incident beam and 60° w.r.t the direction towards the detector.

The observed contrast arises from excitation of oxygen K-edge fluorescence in the VO_x containing parts of the Siemens star. With a beamline energy setting of 533 ± 1.8 eV, the entire bandwidth is above the oxygen K-edge threshold in vanadium oxide. To obtain a homogeneously illuminated image, no sharp absorption features should be present in this chosen excitation bandwidth. The silicon nitride parts remain dark, as shown in Fig. 1(D). The x-ray line focus extends across the entire Siemens star structure in the vertical. The sample is scanned in the horizontal with 1000 steps of 250 nm across the inner part of the Siemens star. At every position, the signal is acquired for 5 s (total measurement duration approximately 96 min, including overhead). Figure 1(C) shows a typical detector image of the fluorescence signal. The structure of the spokes is clearly visible. We highlight a region of interest, which



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Fig. 2. Three-dimensional data set recorded in one monochromator scan and corrected for spaceenergy coupling. The microstructured sample, a group of three thin-film VO₂ squares with an edge length of 30 μ m, is imaged along one dimension (here, *y*). Spatially resolved x-ray emission is recorded in-parallel (*x*, *y* plane), while the incident energy (*z* axis) is scanned. Shown are projections of the 3D data onto each plane, representing traditional RIXS maps (incident versus emitted energies) on the *x*, *z* plane, spatial maps of absorption spectra in the *y*, *z* plane, and spatial maps of emission spectra in the *x*, *y* plane. Isolines and surfaces for a relative intensity of 70% are shown, respectively, as a black line on the projection planes and in a pseudo-3D representation.

is set around the best focus on the detector. The signal within this area is averaged along the *x* direction, yielding the signal for that particular position of the x-rays on the sample {see the dotted line in the reconstruction [Fig. 1(D)]}. This procedure is repeated for every position of the x-ray line focus on the sample resulting in the final reconstruction [Fig. 1(D)].

Fourier ring correlation [23,24] is used to determine the spatial resolution of the RIXS-imaging setup. The correlation of spatial frequencies from two independently recorded images is quantified, and the crossover between signal and noise is determined. The obtained frequency corresponds to a spatial resolution of 1.8 μ m.

Having established micrometer spatial resolution, we acquire RIXS maps from a sample that consists of a 50 nm thin VO₂ film on an Al₂O₃ substrate. The film is structured into squares with an edge length of 30 μ m in groups of three with 10 μ m spacing within the group and 90 μ m spaces between groups. Consequently, the x-ray line focus extends over multiple microsquares in vertical imaging direction.

The monochromator is scanned across the oxygen K-edge excitations in VO₂ from 527 to 536 eV. Because of the bandwidth of ± 1.8 eV, this scan has the effect that every point on the sample is illuminated by x-ray energies between 527 eV + 1.8 eV and 536 eV - 1.8 eV. Each recorded image contains spectral information of the emitted radiation in the horizontal (coordinate x). The signal in the vertical direction (along the focus line) originates from different positions on the sample (coordinate y), each excited by a slightly different incident energy, due to the monochromator dispersion.

The resulting dataset contains emitted intensities as a function of three coordinates: for every monochromator setting, one x, y-detector exposure is recorded. Accounting for the beamline



Fig. 3. (C), (D) RIXS maps created from an $\sim 11 \mu m$ (in the imaging dimension *y*) wide spot on a VO₂ thin film using an analyzer zone plate. (A), (B) RIXS spectra can be obtained by making cuts at fixed incident energies. For the acquisition of (A) and (C), the zone plate focuses elastic emission and moves along with the incident energy. For the acquisition of (B), (D), and (E), the analyzer zone plate focuses the constant-energy fluorescence emission. The trapezoid shape in (C) results from the corrected change of zone plate dispersion. (E) An absorption spectrum is obtained by averaging emitted energies.

dispersion, the vertical spatial sample coordinate y can be decoupled from the incident energy axis z. To visualize the corrected dataset, Fig. 2 shows the three projections of this 3D data onto 2D planes, as well as a 3D-isosurface of 70% relative intensity. RIXS maps showing x-ray emission depending on incident energy can be extracted from different positions of the illuminated sample by slicing this data set in the x, z plane. Furthermore, x, y and y, z slices, respectively, show the spatially dependent x-ray emission and partial fluorescence yield absorption data. In Fig. 3, RIXS maps taken from the center of the microsquares are shown. To increase statistics, the signal is averaged over ~11 μ m on the sample.

As already discussed above, the use of the AZP has the consequence that only a limited range of the emission spectrum is sufficiently focused at a time. For example, accepting a minimum energy resolution of 500 meV allows to use an emitted energy bandwidth $2\Delta E$ of approximately 1060 meV [see Eq. (2)]. To cover a larger emission energy range, the longitudinal AZP position needs to be adapted. This behavior necessitates different strategies when recording RIXS maps with the RIXS-imaging setup: focusing on fluorescence features at constant emission energy requires that the AZP is kept at a fixed position (Fig. 3D). To focus on constant energy transfer features instead, the AZP is scanned along with the incident energy, as shown in Fig. 3(C) for elastic emission. In the latter case, the movement is necessary to adapt the focal length of the AZP to the scanned incident energy. A consequence of the AZP movement is a change in its dispersion, which is compensated for in the data analysis (Fig. 3). Acquisition times for the data shown in Fig. 3 are discussed in Supplement 1.

The strategy to measure RIXS maps with the RIXS-imaging setup is different compared to conventional grating spectrometers, where a full RIXS spectrum from one point on the sample is measured without any scan and a RIXS map is recorded when scanning only the monochromator. With our setup, the strategy of acquiring a complete (one-dimensional) RIXS spectrum (at fixed excitation energy) in focus requires the AZP position to be scanned. However, this directly yields a full RIXS spectrum for every point on the sample, coupled to slightly different excitation energies (2D information). Measuring a 2D RIXS map with a large range of emission energies in focus therefore requires an independent scan of the monochromator and the AZP focus, which in turn directly yields 3D information, i.e., full RIXS maps for all positions along the illuminated part of the sample. The full advantages of parallelization in our setup are realized when RIXS maps for each point on the sample are to be recorded within a small range of emission energies. For such a scheme, the AZP can be kept fixed, and only the monochromator needs to be scanned.

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Comparing the transmission zone-plate-based setup to reflection grating spectrometers, the performance parameters are quite similar: diffraction efficiencies can be optimized for both transmissive and reflective optics for certain energy ranges and are typically on the order of 10%-20% across the soft x-ray range. The achievable energy range is determined largely by the mechanical degrees of freedom. While reflection gratings are often corrected for optical aberrations within a limited energy range, the transmission zone plate is in principle a perfect optic and thus is not limited in the energy range. Practically though, the entrance and exit arm lengths as well as magnification considerations limit the range similarly. The collected solid angle of our AZP setup is 4×10^{-4} sr, which compares with grating collection angles on the order of 4×10^{-5} sr [14]. We stress though that our setup is very forgiving towards angular misalignment of several degrees, while reflection gratings, typically operated at about 2° grazing incidence angle, are very sensitive in this respect [12–15].

Our setup aims at a parallel acquisition at the cost of the narrower emission energy bandwidth that is properly imaged on the detector. In the future, this bandwidth can be increased by using a radially smaller AZP (at the expense of acceptance angle). For instance, reducing the zone plate width from the present 3 to 1.5 mm while keeping the outer radius fixed would result in a substantial reduction in average energy, broadening from 0.94 to 0.37 eV per 1 eV deviation from the energy that is focused (i.e., to about 40%), whereas reducing the size of the aperture of the zone plate reduces the accepted solid angle only to 50%. Depending on experimental requirements, an optimization is possible and can also be chosen *in situ* with movable apertures close to the AZP.

4. SUMMARY

In summary, we demonstrate RIXS measurements with a spatial resolution down to 1.8 μ m with our RIXS-imaging setup based on an off-axis Fresnel zone plate. This measurement technique provides the additional ability to utilize the entire dispersed undulator harmonic without compromising the energy resolution of the spectrometer. As opposed to conventional spectrometers, we can use an x-ray focus line of nearly 1 mm length for efficient in-parallel recording of spatial and spectral information while maximizing the photon flux on the sample and partially compensating for naturally low soft x-ray RIXS cross-sections.

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Disclosures. The authors declare no conflicts of interest.

Supplemental document. See Supplement 1 for supporting content.

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Supplemental Document



Soft x-ray imaging spectroscopy with micrometer resolution: supplement

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Soft X-ray imaging spectroscopy with micrometer resolution: supplemental document

This supplementary document contains an outline of fabrication processes (section 1) of the microstructured samples and the zone plate optics together with further references. Furthermore, the derivation of Equations (1) and (2) from the main publication is detailed in section 2.

1. FABRICATION OF ZONE PLATE OPTICS AND MICROSTRUCTURED SAMPLES

Zone plates

Both the linear illumination zone plate (IZP) and the off-axis analyzer zone plate (AZP) are fabricated by high-resolution electron beam lithography, as described in [1, 2]. In essence, a hydrogen silsesquioxane film is deposited on a 100 nm silicon nitride (Si_3N_4) membrane via spin-coating. The zone plate structures are then created with the electron beam.

The IZP has an aperture of $3.8 \text{ mm} \times 1.9 \text{ mm}$ (v×h) and an outermost zone width of 184 nm. The zones consist of 110 nm thick nickel structures on a 100 nm silicon nitride membrane with a 10 nm thin gold layer in between the membrane and the nickel structures. At a photon energy of 530 eV, the bandwidth of 3.6 eV causes a variation of the focal length of $\pm 0.5 \text{ mm}$ around 149.3 mm. Since the length of the focus line on the IZP is approximately 1 mm, an IZP tilt-angle of $\sim 45^\circ$ focuses the incident bandwidth in the sample plane to less than 1 µm in width. This effectively reduces the vertical aperture to 2.7 mm.

Vanadium oxide Siemens star sample

The fabrication of the Siemens star structures follows a similar procedure as the zone plate fabrication. Instead of a silicon-based resist material, a vanadium-based metal-oxide cluster is used as precursor material, exposed to electrons in an electron beam lithography system, and developed with a 1 % solution of HCl in isopropanol.

Microstructured vanadium dioxide thin-film sample

The vanadium dioxide films were deposited on Al₂O₃ (10-10) single crystal substrates by pulsed laser deposition (PLD), using a commercially available sintered ceramic V₂O₅ target. During the deposition process, the substrates were kept at a temperature of 630 °C in an oxygen atmosphere of 10^{-2} mbar. The PLD system uses a krypton fluoride (KrF) excimer laser of 248 nm wavelength. The laser fluence was 2 J/cm² at a pulse repetition rate of 1 Hz. The microstructures consisting of groups of nine squares, each measuring 30 µm × 30 µm were fabricated using optical lithography and ion beam etching. See also [3, 4].

2. DERIVATION OF ZONE PLATE DISPERSION FOR ENERGIES WHICH ARE OUT-OF-FOCUS

The following demonstrates the derivation of Equations (1) and (2) in the main publication, which express the energy and spatial resolution of energies which are not perfectly focused by an off-axis analyzer zone plate (AZP). This derivation expands on work published in [1].

Zone plates are chromatic, which may pose a problem if incident X-rays are of a certain bandwidth (as is the case when zone plates are used as analyzers in an emission spectrometer). This situation is depicted in Figure S1: an AZP focuses energy E_0 (red) at the image distance b_0 . Consequently, higher energies E' (blue) are then focused at an image distance $b' > b_0$. If a detector is located in focus of E_0 at the distance b_0 from the AZP (as shown in Figure S1A), the signal of the energy E' will be defocused. The aim of the derivation presented here is to find expressions for the rate at which energy resolution and spatial resolution degrade for slightly defocused energies, and to express dependencies on zone plate design parameters.

Starting from the zone plate equation (S1), we will find an expression for the change of dispersion with energy. The zone plate equation directly expresses the chromaticity of a zone plate:



Fig. S1. Zone plate chromaticity. Schematic view of an off-axis zone plate which focuses different energies. The focal length of a zone plate is longer for higher energies (E', represented in blue) and shorter for lower energies (E_0 , represented in red). Moving the detector to different positions along the optical axis (A, B and C) allows selecting the energy content which is focused. Schematic detector images for the different positions are shown in the upper right corner. Defocused energies lead to a rectangular spot on the detector since they image the square aperture of the off-axis zone plate.

$$r_n \cong \sqrt{n\lambda f} \Longleftrightarrow f \propto E$$
 (S1)

Here, λ is the incident photon wavelength, f is the focal length of the zone plate, E is the photon energy, n is the number of filled and empty zones and r_n is the radius of the n^{th} zone. With the overall number of zones N, $r_N = r_{\text{out}}$ is the outer radius of the zone plate.

In Figure S1, the position A of the detector depicts the situation in which the zone plate focuses energy E_0 (red) onto the detector. The signal of the photon energy $E' = E_0 + \Delta E$ (blue) is already defocused to a size Δx , centered around position x in the dispersive direction on the detector. According to the intercept theorem, a geometric consideration leads to (see Figure S1):

$$\frac{x}{\Delta b} = \frac{r_n}{b'} \iff x = r_n \left(1 - \frac{b_0}{b'} \right) \tag{S2}$$

Furthermore, the lens maker's equation expresses the dependence of the image distance b on the focal length f and the object distance g (fixed by the geometry of the experiment):

$$\frac{1}{b} = \frac{1}{f} - \frac{1}{g} \tag{S3}$$

Combining Equations (S2) and (S3) yields an explicit expression of the dependence of the position on the detector, *x*, on the energy *E*:

$$x(E) = r_n \cdot \left[1 - b_0 \left(\frac{1}{f} - \frac{1}{g} \right) \right]$$

= $r_n \cdot \left[1 - b_0 \left(\frac{1}{C \cdot E} - \frac{1}{g} \right) \right]$
 $\approx x(E_0) + \left. \frac{\partial x}{\partial E} \right|_{E=E_0} \cdot \Delta E + \cdots$ (S4)

Here, $f \propto E$ (form Equation S1) is used, introducing a proportionality factor $C = \lambda f/hc$, which is constant for a given zone plate design. In the last step in Equation (S4), a Taylor expansion around the energy E_0 is used, which, for small ΔE , can be truncated after the linear term. For fixed positions of sample, AZP (distance g) and detector (at distance b_0 to AZP) the dispersion $\partial x/\partial E$ can be evaluated:

$$\frac{\partial \left(x\left(E\right)\right)}{\partial E}\Big|_{E=E_{0}} = \left.\frac{\partial}{\partial E}\left\{r_{n}\cdot\left[1-b_{0}\left(\frac{1}{C\cdot E}-\frac{1}{g}\right)\right]\right\}\Big|_{E=E_{0}} = \frac{r_{n}\cdot b_{0}}{C\cdot E_{0}^{2}} = \frac{r_{n}\cdot b_{0}}{f\cdot E_{0}}$$
(S5)

Moreover, together with the lens maker's equation (S3) and the magnification $M = b_0/g$, this yields:

$$\frac{\partial \left(x\left(E\right)\right)}{\partial E}\Big|_{E=E_{0}} = \frac{r_{n}}{E_{0}}\left(M+1\right)$$
(S6)

Equation (S6) yields the dispersion for a single ray diffracted from one spot on the AZP (which is defined by r_n) and expresses a relation of the position r_n on the AZP to the position x on the detector. A mean dispersion $\partial \bar{x}/\partial E$ is obtained from a mean off-axis zone plate radius $\bar{r} = (r_{\text{out}} + r_{\text{in}})/2$. Correspondingly, by using the (radial) zone plate width $w = r_{\text{out}} - r_{\text{in}}$ in Equation (S6), the change of the spot size Δx on the detector with energy can be expressed.

The spot size on the detector Δx_{Det} for an energy deviating from the focus energy E_0 by ΔE is obtained by combining Equation (S6) with Equation (S4):

$$\Delta x_{\text{Det}} \cong w \frac{\Delta E}{E_0} \left(M + 1 \right) \tag{S7}$$

Since this describes the spot size on the detector, the spatial resolution at the position of the sample Δx_{Sample} is obtained by additionally dividing Equation (S7) by the magnification, which leads to Equation (S8), which is Equation (1) in the main publication.

$$\Delta x_{\text{Sample}} = w \frac{\Delta E}{E_0} \cdot \frac{(M+1)}{M}$$
(S8)

Finally, the energy resolution d*E* is obtained from the spatial resolution by division by the mean dispersion $\partial \bar{x}/\partial E$ (see Equation (S6)).

$$dE = \frac{w}{\bar{r}} \cdot \Delta E \tag{S9}$$

Table S1 lists the parameters for our setup which we used to calculate exemplary values from Equations (1) and (2) in the main manuscript (i.e. Equations (S8) and (S9)).

 Table S1. Experimental and analyzer zone plate (AZP) parameters used in Equations (1) and (2).

Parameter	Symbol	Value
center energy	E_0	530 eV
deviation from center energy	ΔE	1 eV
AZP radial width	w	3 mm
AZP mean radius	ī	3.2 mm
AZP magnification	М	11.5

3. MEASUREMENT ACQUISITION TIMES

For the data shown in Figure 3 C (D), the acquisition time per step was 30 s (60 s), resulting in a total measurement time of about 20 min (40 min).

If the sample was homogeneous, a single acquisition of 30 s (60 s) would be sufficient for a RIXS map with 3.6 eV incident energy bandwidth and an emission energy bandwidth of 2 eV with an energy resolution below 1 eV. Utilizing the bandwidth, the full map shown in Figure 3 C (D) could have been recorded with three steps of the monochromator, i.e. within one and a half and three minutes, respectively. Additionally, resolving the whole fluorescence spectrum of about 6 eV bandwidth with a resolution better than 1 eV would have required three steps of the AZP yielding a total acquisition time of nearly 5 min (10 min).

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3.2.2 Vanadium Dioxide (VO₂) Microsquares

The previous section 3.2.1 and Paper I [1] introduced RIXS imaging as a method to perform soft X-ray spectromicroscopy experiments with a spatial resolution down to about $2 \,\mu\text{m}$. To further develop the RIXS imaging method, we chose small VO₂ thin-film structures as sample to test the capabilities of the method to observe a phase transition on the micrometre length scale.

 VO_2 is a long-known [22], widely studied [27, 28] example for a quantum material with a pronounced IMT around 360 K (see also Figure 2.2), not far away from room temperature. The phase transition is characterized by a change of both the lattice and the electronic structure. The metallic, high-temperature phase has a rutile crystal structure (*R*-phase) that, upon transition, is distorted and decreases its symmetry when pairs of vanadium atoms dimerise to form the monoclinic, insulating M_1 phase. Energies of the electronic bands formed by the vanadium 3*d*- and oxygen 2*p*-orbitals change so that a band gap of about 0.7 eV opens around the Fermi level [23]. Because the unoccupied electronic bands change in energy, XAS is ideally suited to follow the IMT.

The fact that both the electronic and crystallographic structures change during the transition has sparked a long-standing debate whether the electronic or the lattice change is the driving force of the IMT, which is also referred as a competition of Peierls instability vs. Mott transition [24, 25, 27, 28, 100, 101, 248], see section 2.1.1. This long-standing debate may - at least partially - be caused by a complex phase diagram of VO_2 around the transition temperature: Besides the insulating M_1 phase, other insulating phases (the monoclinic M_2 and the triclinic T phases) with distinct crystallographic structures have been reported in VO_2 , induced by Cr-doping [249] or application of uniaxial strain [250]. Even a solid-state triple point comprising the M_1 , M_2 and R phases has been observed [251] at precisely the IMT temperature. These phases can coexist in VO_2 with typical sizes on the few-hundred nanometre scale [97, 104, 226, 252]. The fact that inhomogeneities close to the micron scale occur around the phase transition makes it reasonable to assume that structuring VO_2 on length scales close to the domain size might influence the phase transition kinetics. Indeed, it has been shown that the transition temperature, at which the IMT takes place, can change by up to 15 K when sample or structure sizes are scaled down to the micro- and nano-scale [253–257].

Therefore, VO₂ microscqares can be considered a good benchmark sample for the RIXS imaging method, which is expected to observe the IMT in single $30 \,\mu\text{m} \times 30 \,\mu\text{m}$ squares by measuring PFY-XAS. This endeavour was successful - and an even more interesting effect could be observed: The transition temperature for the IMT is lower at the edges of said squares in comparison to the centres. This effect is highly relevant for the design of microelectronic devices, because it highlights how physical properties of bulk materials are not preserved when they are structured on the micro-scale and because VO₂ is a promising candidate for application in electronic devices [27, 28, 56, 258, 259].

Understanding the driving mechanisms behind the phase transition in VO_2 will require methods that are able to probe these phases individually [99]. This is currently not achieved with the resolution of 1.8 µm of the RIXS imaging setup. Instead, we measured the volume-fraction-averaged domain response. Nonetheless, we could observe spatial dependencies of the transition temperature within the microsquares. An improvement of the magnification (as shortly discussed in the previous section 3.2.1) by a factor of 5 or more will enable true domain-resolved studies with our setup, allowing to resolve real-space dynamics of domain formation during the IMT in VO₂.

In the following paper³, entitled "Microstructure effects on the phase transition behavior of a prototypical quantum material", an X-ray absorption imaging study of the thermally driven IMT in VO₂ microsquares using the RIXS imaging setup described in Paper I [1] (section 3.2.1) is presented.

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OPEN Microstructure effects on the phase transition behavior of a prototypical quantum material

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Materials with insulator-metal transitions promise advanced functionalities for future information technology. Patterning on the microscale is key for miniaturized functional devices, but material properties may vary spatially across microstructures. Characterization of these miniaturized devices requires electronic structure probes with sufficient spatial resolution to understand the influence of structure size and shape on functional properties. The present study demonstrates the use of imaging soft X-ray absorption spectroscopy with a spatial resolution better than 2 µm to study the insulatormetal transition in vanadium dioxide thin-film microstructures. This novel technique reveals that the transition temperature for the conversion from insulating to metallic vanadium dioxide is lowered by 1.2 K ± 0.4 K close to the structure edges compared to the center. Facilitated strain release during the phase transition is discussed as origin of the observed behavior. The experimental approach enables a detailed understanding of how the electronic properties of quantum materials depend on their patterning at the micrometer scale.

Quantum materials are characterized by exotic physical properties arising from correlations and inter-dependencies of electron spin, charge and orbital degrees of freedom, as well as the lattice. The interaction of these subsystems results in intriguing functional properties like high-temperature superconductivity or insulator-metal transitions¹⁻³. Current and future devices require patterning of such materials on the micro- or nanometer scale. Designing such devices requires an understanding of how bulk material properties are preserved or altered across these miniaturized structures since, e.g., the relatively enlarged surface areas can facilitate volume strain relaxation. Strain effects become even more important when the functionality of the device is derived from solid-solid phase transitions, like insulator-metal transitions, during which changes of lattice parameters occur. For example, strain in thin-films, mediated via the substrate, has been observed to significantly affect the phase transition temperature^{4,5}.

In quantum materials research, vanadium dioxide (VO₂) is a prototypical insulator-to-metal transition (IMT) compound with a transition temperature T_t of approximately 340 K⁶. The proximity of this solid-solid phase transition to room temperature along with a change in resistivity of up to five orders of magnitude makes VO2 a particularly interesting compound for applications (see⁷ and references therein), e.g., as a phase change material in optical waveguide switches⁸, for optical⁹ or memristive^{10,11} devices, thermal sensors or thermochromic coatings¹² on multifunctional windows¹³, as well as neuromorphic circuits¹⁴.

On the microscopic level, the IMT in VO_2 is characterized by a combined change of crystallographic and electronic structure. The metallic high-temperature phase of VO₂ has a rutile crystal structure. According to the Goodenough model¹⁵, the crystal symmetry decreases upon cooling of the material when two adjacent vanadium atoms move closer toward each other, forming a monoclinic lattice. The valence and conduction bands in VO2

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are formed by hybridization of vanadium 3*d* and oxygen 2*p* orbitals. In the metallic phase, the conduction band consists of directional $d_{||}$ and unidirectional π^* bands¹⁶. Due to the dimerization during the formation of the insulating phase, the $d_{||}$ band splits into bonding $(d_{||})$ and antibonding $(d_{||})$ contributions, and the π^* band is lifted in energy. These electronic structure effects jointly cause the opening of a band gap around the Fermi level.

X-ray absorption spectroscopy (XAS) probes the unoccupied density of states. The shift of unoccupied bands during the IMT thus makes XAS an ideal and routinely used tool to follow the IMT in VO₂¹⁶⁻¹⁹. In particular, XAS at the oxygen K-edge probes the 1s - 2p transition in oxygen, making it most sensitive to the nature of the phase of VO₂¹⁶. We note that a different monoclinic, insulating phase (termed M_2), has been proposed for strained or Cr-doped VO₂ samples²⁰⁻²². To our knowledge, no X-ray absorption spectra of this phase are known. Thus, our analysis omits a potential influence of this phase.

In VO₂ thin-films, it has been observed that the IMT progresses via domain formation in the vicinity of the transition temperature T_t^{23-26} . Across a large temperature range of up to 50 K around T_t , insulating and metallic domains coexist²⁵. Upon heating, metallic islands form, grow and build a domain network within the insulating phase. The size of these domains typically is on the sub-micron scale^{24,25,27}. Therefore, structuring VO₂ thin-films on the micrometer length scale, as required for devices, naturally influences the domain network. In literature, different forms of micro- and nano-structuring have been shown to alter T_t by approximately 5 K to 15 K²⁸⁻³². However, the question whether this happens homogeneously across the structures has not yet been addressed.

Results

In this study, we use imaging soft X-ray absorption spectroscopy with a spatial resolution of down to $1.8 \,\mu$ m to investigate the thermally driven IMT in supported thin-film VO₂ squares of $30 \,\mu$ m × $30 \,\mu$ m size (see Fig. 1). In brief, the combination of imaging and spectroscopy is realized with an off-axis Fresnel zone plate between sample and two-dimensional CCD detector. The zone plate is used to image and disperse X-ray emission simultaneously onto orthogonal dimensions of the detector^{33,34}. As a measure for the X-ray absorption, we observe oxygen *K*-edge fluorescence within an emission energy window of 526.5 eV ± 2.5 eV. A more detailed characterization of the experimental setup can be found in a previous publication³⁵.

With the beamline optics and a linear illumination zone plate, incident X-ray radiation is focused onto the sample as a vertical line of approximately 970 μ m length and sub-micron width. Due to dispersion by the beamline monochromator, the photon energy along the line focus changes linearly by approximately ± 1.8 eV, centered around the monochromator energy.

The sample is a bulk-supported 50 nm thin microstructured VO₂ film (see Experimental section and the reference³⁶). The structures are squares with an edge length of 30 μ m, arranged in groups of three by three (see Fig. 1). The X-ray line focus extends across several groups of VO₂ microsquares. Figure 1 shows a typical, background subtracted detector image. The horizontal is the dispersive direction of the analyzer zone plate and thus shows the fluorescence on an emission energy axis. The vertical is the imaging direction of the analyzer zone





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plate and thus encodes vertical position on the sample surface as well as the systematic incident energy variation. The signal of three groups, each containing three microsquares, can be clearly recognized.

In order to investigate to which extent patterned thin-films exhibit inhomogeneous phase transition behavior, temperature series of X-ray absorption spectra are recorded by scanning the incoming photon energy across the oxygen K-edge from 527 to 536 eV for nine different temperatures from 339 to 351 K (i.e., in steps of 1.5 K). In the imaging direction, the signal from edge and center regions of the microsquares is analyzed separately in regions of interest (ROIs) of 4.5 μ m and 12.3 μ m height close to the edges of the squares and in the square centers, respectively. Between the center region and each edge region, a spacing of 4.4 μ m was excluded from the analysis. Exemplary ROIs for edges and centers are shown for one square in Fig. 1. Data presented hereafter is derived from the evaluation of the second to sixth square (counted from top to bottom) with corresponding ROIs. The other squares moved out of the X-ray focus during the experiment when the sample holder expanded due to the increase in temperature. For the evaluated squares, the signal within each ROI is integrated and plotted against the incident energy (corrected for the monochromator dispersion along the line focus) resulting in the partial fluorescence yield X-ray absorption spectra shown in Fig. 2.

The spatially resolved X-ray absorption spectra, extracted from edge and center regions of the VO₂ microsquares for different temperatures around T_t show very good agreement with spectra from literature^{19,37–39}. In the case of center regions, this is true for all spectral features and the corresponding temperatures, while in the case of edge regions, deviations are observed for the temperature dependence. Upon heating, the largest changes in the oxygen *K*-edge absorption spectra induced by the IMT are found in two spectral regions: intensity of the $d_{||}$ shoulder at 530.3 eV is decreased and the leading edge of the π^* peak between 529 and 530 eV is red-shifted. Systematic changes continue towards higher temperatures beyond the presently studied temperature range. Despite statistical uncertainties, we already observe that these spectral changes upon heating occur earlier in the regions close to the edge of the microsquares as compared to regions in the center. In the right panel of Fig. 2, we display further evidence for this observation, gaining statistical significance by averaging in the relevant regions: The average spectral intensity increase in the π^* region and the intensity decrease in the $d_{||}$ region with increasing temperature are both more advanced for the edges (red) in comparison to the centers (black). As a guide to the eye, linear fits of the edge evolutions (red, dash-dotted line) are shown alongside the data and linear fits of the center evolutions (black dashed lines) and vice versa.

Analysis

With the given spatial resolution of $1.8 \,\mu$ m, we can assume that each spectrum contains contributions from metallic and insulating domains. In the case of extended VO₂ thin-film layers, the domain size has been shown to be hundreds of nanometers in size^{25,27}, and we can expect a similar domain size also in the edge regions of the squares. When the VO₂ sample is heated across the IMT, the measured signal is thus an average of the relative contributions from the continuously growing, respectively shrinking, metallic and insulating domains. In consequence, spectral changes observed in XAS do not resolve an abrupt 1st order IMT but are continuous with

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Figure 3. Comparison of average metallic fraction of center (black filled squares) and edge (red empty squares) regions of VO₂ microsquares for experimental temperatures around the transition temperature T_t . Each data point in panel (**a**) is the average of seven metallic fractions, determined from different energies in the X-ray absorption spectrum (see Fig. 2). Error bars represent the standard deviation of those seven values. The dashed black line is a guide to the eye and represents a perfectly linear increase of the metallic fraction with experimental temperature. The inset visualizes the regions of interest (ROIs) on a VO₂ square from which the signal for respective data color was extracted. In horizontal direction the dimensions of the ROIs are determined by the width of the vertical X-ray line focus. In the vertical, the ROI dimensions are chosen. The blue shaded area shows the difference in metallic fractions of center and edge regions, which is additionally plotted in panel (**b**). The black and red horizontal line in **b** are a guide to the eye at difference values of 0% and 3%.

temperature. The spectra provide a measure for the fraction of the sample which has undergone the IMT, which we refer to as metallic fraction. For a quantification of the metallic fraction, we refer to recent X-ray absorption measurements at the oxygen *K*-edge, where quasi-linear IMT-induced changes over a temperature range of approximately 40 K have been reported³⁸. The low-temperature onset was observed at 335 K in our setup, which deviates slightly from the reported one³⁸. We attribute this to different positions of temperature sensor and sample. Accordingly, we assume the metallic fraction to increase linearly from 0 at 335 K to 1 at 375 K.

Analysing the characteristic changes in the π^* and $d_{||}$ spectral regions then allows us to directly extract the fraction of metallic VO₂ in the sample. We assume that the spectra from the center regions are showing the same temperature dependence as the spectra from unstructured films. We further assume that both the metallic fraction as well as the spectral changes are linear in temperature. Thus, we can extract the metallic fraction directly from the spectra and apply the same analysis procedure also to the spectra from the edge regions to quantify the deviations.

In detail, we connect spectra to the fraction of metallic VO₂ as follows: Within the energy region with the most prominent spectral changes around the π^* -peak from 529 eV to 531 eV, we select seven intensity data points $I(E_i, T)$ from the center region measurement marked by gray dashed lines in Fig. 2. The intensity-temperature relations of the center region data points are mapped to intensity-metallic fraction relations using the assumed linear dependence of temperature and metallic fraction for unstructured thin films (see above). These seven relations are linearly fitted and yield a set of parameters which allows to determine the metallic fraction of any other spectrum evaluated from the measured intensities at these energy points. The obtained seven values are then averaged. We note that the region around the maximum of the π^* -peak at 529.9 eV shows no temperature dependence and is thus not sensitive to the changes in metallic fraction. This region was excluded from the analysis.

Discussion

The resulting average metallic fractions for all measured spectra are shown in Fig. 3A. The black and red data points in Fig. 3A show the average metallic fraction for the temperature series of the microsquare center and edge regions. Within the experimental uncertainty, the fraction of metallic domains is consistently larger at the edge regions of the VO₂ squares in comparison to the center regions for the temperature range studied in this work. The average metallic fraction at the edge regions also shows the same curved deviation from linearity as the center regions, but with an offset of 3 ± 1 percentage points on average (Fig. 3B). A change of metallic fraction of 3 ± 1 percentage points translates to a temperature difference of $1.2 \text{ K} \pm 0.4 \text{ K}$. Upon heating, the edge regions thus reach the same state (metallic fraction) in the the phase transition as the centers at a $1.2 \text{ K} \pm 0.4 \text{ K}$ lower temperature. This value is independent of the chosen scaling of the metallic fraction. We emphasize that
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both center and edge regions are measured at the same time under the same sample conditions. Furthermore, we found no systematic deviation between different squares.

Some previous reports have examined the effects of structure size on the transition temperature of VO₂ micro- and nanostructures and reported two opposing trends: On the one hand, studies of size effects in VO₂ nanoprecipitates, prepared in a SiO₂ substrate by ion implantation and subsequent high-temperature annealing²⁹, as well as of VO₂ nanoparticles capped with gold⁴⁰, report a widening of the IMT hysteresis with decreasing particle size, i.e., smaller particles with larger relative surface area show on average higher transition temperatures T_t upon heating and lower T_t upon cooling. These results are at odds with our data, where edge regions with increased surface area show a lower transition temperature upon heating.

On the other hand, different reports on VO₂ nano- and microstructures are consistent with our findings: For VO₂ nanowires on a SiO₂ surface, the transition temperature is lowered upon heating for thinner nanowires³¹, i.e., for larger relative surface area. A similar trend is observed on rod-like VO₂ nanostructures of subsequently smaller sizes³⁰, for nanowires between 3.5 μ m and 100 nm width on a Si wafer²⁸ and for films with varying grain size³². This effect is commonly attributed to an enriched defect (i.e., nucleation site) density at the surface, which, for smaller structures, is larger with respect to the bulk. The contradicting results^{29,40} (i.e., more surface area leading to an increased transition temperature upon

The contradicting results^{29,40} (i.e., more surface area leading to an increased transition temperature upon heating) likely originate from the surface treatment of the VO₂ structures, as they were either implanted in a SiO₂ matrix in the first case or capped with gold in the second case. As a result, surface bonds could be saturated and substantially fewer defects were potentially formed at the surface of the VO₂ nanostructures.

The VO₂ microstructures which we report on here are also expected to possess a higher defect density, such as oxygen vacancies⁴¹⁻⁴³, at the edge regions of the squares, arising for example from the etching process during structuring of the sample. However, we do not consider enriched nucleation site density at lateral edges to play a substantial role during the phase transition of our microsquares. Firstly, by far the biggest contribution to the outer boundaries of these structures comes from the film top surface which is parallel to the substrate. The lateral edge surfaces increase the total surface area of the measured edge region only by less than 1%. Secondly, we assume that the higher defect density influences only the first few layers of the crystal. The ROI of the edges in which we observe the IMT at lower temperatures, however, was set to measure 4.5 μ m in width, which corresponds to around 10,000 layers. Thus, by averaging within this ROI, higher defect site density at the lateral edge regions becomes negligible in comparison to the volume effects. This is further supported by the observation that, within the experimental sensitivity, the slope of the metallic fraction over temperature (Fig. 3A) is unchanged between center and edge regions. On the contrary, a change in the local distribution of nucleation centers would be expected to promote a faster completion of the IMT (i.e., a steeper slope in the metallic fraction-temperature diagram), rather than the observed shift of the overall phase transition temperature.

Thus, we assume a different cause for the different transition temperatures of edge and center regions: Strain, induced by a change in crystal lattice constants during the phase transition, can add up across micrometers^{44,45}. In our experiment, strain relaxes more easily at the edge regions in comparison to the more-confined center regions. Strain changes the potential energy landscape and thus the energy balance of the subsystems driving the IMT, which apparently leads to an earlier onset of the IMT with a similar slope as a function of temperature. Thus, we assess that an eased strain relaxation at the edge regions could lead to the overall lowering of the transition temperature by 1.2 K \pm 0.4 K on average. Moreover, we assume that the effect of facilitated strain release on the transition temperature is much larger at the microsquare edges and decreases toward the center.

Conclusions

In summary, we have utilized X-ray imaging spectroscopy with micrometer resolution for the characterization of the insulator-metal transition in $30 \,\mu\text{m} \times 30 \,\mu\text{m}$ sized VO₂ thin film structures. Quantitative comparison of the phase transition-induced shift in the X-ray absorption spectra at the oxygen *K*-edge revealed that the transition temperature upon heating was lowered by $1.2 \,\text{K} \pm 0.4 \,\text{K}$ at the edge regions of microstructures in comparison to center regions. Our findings suggest an eased release of strain which is built up during the crystallographic phase transition. These results demonstrate how shape and pattern influence the functional properties of materials on the microscale. Systematic studies of phase transitions of microscopically patterned quantum material systems will be indispensable in order to be able to accurately tailor functional devices. Future studies with improved spatial resolution will furthermore enable a more detailed analysis of the length scales involved in the build-up and release of strain during solid-solid phase transitions.

Methods

Imaging soft X-ray absorption spectroscopy measurements. Spatially resolved X-ray absorption partial fluorescence yield measurements were performed with the MUSIX endstation⁴⁶ located at the soft X-ray beamline P04⁴⁷ of the synchrotron storage ring PETRA III at DESY in Hamburg. Characteristics of the setup are discussed in the reference³⁵. The setup makes use of the entire bandwidth that is transmitted through the beamline monochromator. A 1200 lines mm^{-1} grating was used and the exit slit was opened as far as possible (2.9 mm). At 530 eV photon energy, the monochromator dispersion was approximately 1.3 eV mm^{-1} , leading to the transmitted bandwidth of ± 1.8 eV, mentioned in the main text. The refocusing mirrors downstream of the monochromator were used to focus the dispersed beam only in the horizontal direction. The vertical focal point of the refocusing mirrors was several meters downstream of the sample. The vertical line focus was instead created with a linear illumination zone plate to create a narrower line focus than possible with the refocusing mirrors. The illumination zone plate was located about 15 cm upstream of the sample. As a result, a sub-micron wide vertical focus line of approximately 970 µm length was obtained. Along the direction of the vertical line focus, the sample was imaged with an off-axis zone plate, which additionally dispersed X-ray semitted from the

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sample in horizontal direction. Object and image distances were 15 cm and 172.5 cm respectively, resulting in a sample magnification of 11.5. Movement of the off-axis zone plate along the sample-detector axis allows focus-ing different energies of the emission spectrum onto the CCD detector. The detector was a CCD camera (Andor iKon) with a pixel size of 13 μ m. An aluminium foil was used to protect the detector from visible light.

For the X-ray absorption measurements, the central photon energy was scanned around the oxygen *K*-edge from 527 to 536 eV. Because of the bandwidth transmitted through the open exit slit, every point on the sample is illuminated by photon energies between 527 eV + 1.8 eV and 536 eV – 1.8 eV. The photon energy was scanned in steps of 0.25 eV with 60 s integration time per step, resulting in less than 40 min acquisition time per temperature. Between absorption scans, the sample temperature was increased from 339 to 351 K in steps of 1.5 K. After each temperature increase, the sample was given 40 minutes of equilibration time.

Sample fabrication. The 50 nm thin vanadium dioxide film was deposited on a commercial Al_2O_3 (0001) single crystal substrate (supplied by Shinkosha, Japan) by pulsed laser deposition, using a KrF excimer laser of 248 nm wavelength and a commercial sintered ceramic V_2O_5 target (supplied by Evochem, Germany). The laser fluence during deposition was 2 J cm⁻². The structures were created using optical lithography and ion beam etching. The etching process was monitored using a secondary ion mass spectrometer. Etching was stopped after the part of the VO_2 film that was not protected by the photo resist was removed entirely.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Author contributions

M.B., C.D. and K.R. conceived and supervised the project. J.O.S., F.D., B.R. J.B., R.Y.E., P.S.M., S.K.M., M.H., C.S.L. and M.B. performed the synchrotron measurements. F.D., B.R. and C.D. fabricated the zone plate optics. A.P. and H.K. designed and fabricated the microstructured VO_2 thin-film sample. J.O.S. analyzed the data and interpreted it together with C.S.L., K.R. and M.B.; J.O.S., C.S.L. and M.B. wrote the manuscript with input from all co-authors.

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Additional information

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3.2.3 Soft X-ray Full-field Diffraction Imaging with Micrometer Resolution

Paper III [3] presents another application of a setup derived from the RIXS imaging method. The schematic setup is shown in the centre panel in Figure 3.1: The off-axis zone plate is used to image the sample, and diffraction of the sample is recorded. In principle, this experiment could be done with a full zone plate, but the advantage of an off-axis zone plate is that the desirable first order diffraction is well separated from the zeroth order diffraction. The off-axis zone plate was placed into the direction of the (011) Bragg peak of the sample and XRD was recorded.

YTiO₃ [46], which is the parent compound of $Y_{1-x}Ca_xTiO_3$, the subject of Paper III [3], is an example for a typical Mott insulator [46]. Because of the Ti- d^1 electronic configuration, only the energetically lowest d_{xy} orbital⁴ is singly occupied. This is also the reason why YTiO₃ is ferromagnetic. However, the system is not metallic because this half-filled d_{xy} -band occupation leads to an increase in Coulomb repulsion and localization of the electron at the Ti³⁺ sites, making the YTiO₃ system insulating as described in section 2.1.1. In this case, a transition to the metallic state can be induced by replacing trivalent yttrium atoms with divalent calcium. This will lead to Ti³⁺ atoms becoming Ti⁴⁺ with an empty *d*-shell. With increased concentration, the system is driven away from the half-filled *d* band configuration until at doping levels of about 37% (i.e. $Y_{0.63}Ca_{0.37}TiO_3$), the transition to the metallic state is induced [46].

Two aspects make this experiment especially interesting: First, the sample shows several phases and transitions between them: At low and high temperatures, two orthorhombic phases exist, respectively referred to as low-temperature orthorhombic (LTO) and high-temperature orthorhombic (HTO). Additionally, a low-temperature monoclinic (LTM) phase coexists with the LTO phase with varying relative volume fractions [260]. The LTO phase is thought to contribute to the observed metallic property of $Y_{1-x}Ca_xTiO_3$ at low temperatures [260], whereas the LTM phase is of insulating character [260]. In the monoclinic phase, charge ordering of Ti³⁺ and Ti⁴⁺ ions leads to the emergence of Bragg diffraction from the (011) peak, which is forbidden in the unordered orthorhombic phase [261, 262], making the diffraction very sensitive to only the monoclinic phase.

Second, by making the X-ray focus on the sample large, full-field diffraction imaging could be realized. In the vertical, the exit slit was entirely opened. In combination with the high photon flux delivered by the soft X-ray beamline P04 at PE-TRA III [229], this resulted in a high number of photons of approximately 3×10^{14} on the sample, allowing to record diffraction images from about one square millimetre of sample in 1 s to 3 s. This allowed scanning the entire sample at several temperatures. By combining the high potential of this method with such an interesting and ideally-suited sample, we found coexisting stripe domains extending across more than a millimetre - and relate them to variations of the chemical composition in the sample by means of energy-dispersive X-ray spectroscopy (EDX).

In the following paper, entitled "Stripes from chemical inhomogeneity in floating-

⁴Due to the orthorhombic crystal field, the degeneracy of the *d*-orbitals in the atomic case is lifted and the d_{xy} orbital becomes the energetically most favoured.

zone grown rare-earth titanates", we present a study of stripe domains in $Y_{1-x}Ca_xTiO_3$ and, to our knowledge for the first time, show experimental prove that these stripes emerge due to chemical inhomogeneity.

Stripes from chemical inhomogeneity in floating-zone grown rare-earth titanates

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Abstract

Hole-doping the Mott-insulator yttrium titanate (YTiO₃) with calcium ions induces an insulator-metal transition and results in a complex phase diagram. Lowering the temperature of $Y_{0.63}Ca_{0.37}TiO_3$ from room temperature leads to the observation of two subsequent crystallographic phase transitions as well as a transition between metallic and insulating phases, driven by phase separation. In this study, we present measurements on this material using a soft X-ray imaging approach with a spatial resolution of 2 µm. The image is generated by observing diffraction from the (011) plane that is selective to charge-ordered monoclinic areas, characteristic for the insulating phase. In large temperature ranges, we observe a curved stripe pattern of the insulating phase with a period of 13 µm and lengths of more than a millimeter. From local elemental analysis in a scanning electron microscope, we find the same pattern in small variations of the doping concentration, consistent with the observed temperature variation in the local phase appearance. Such variations are unexpected in the used floating-zone single crystal growth method, but a more general occurrence may be implied. Further studies might yield control over the stripe formation, which allows to tailor macroscopic effects, like anisotropic conductivity in the future.

1 Introduction

The perovskite and ferromagnetic insulator ATiO₃ (with A being a trivalent rare earth ion or Y^{3+}) is a prototypical Mott-Hubbard insulator and as such has been subject to extensive studies on strongly correlated electron systems (1, 2). It possesses an electronic d^1 structure. The splitting induced by the orthorhombic crystal field leads to a half-filled d_{xy} band. With a single electron at every site, Coulomb repulsion is maximized, making this configuration a classical case for a Mott-insulator (2). By substituting the trivalent A^{3+} with a divalent ion B^{2+} , one hole per Ti atom can be induced, thereby changing the Ti electronic structure from d^1 to d^0 . The doping concentration x in $A_{1-x}B_xTiO_3$ represents the hole concentration and the *d* band filling is given by d^{1-} x (2). By decreasing the *d*-band filling, the Coulomb repulsion is reduced and the insulator-to-metal transition (IMT) can be induced. The concentration x at which the transition occurs depends on the divalent and trivalent ions: For example, in $La_{1-x}Sr_xTiO_3$, several percent of doping are sufficient to induce the IMT, whereas in $Y_{1-x}Ca_xTiO_3$, the ferromagnetic order vanishes around $x \sim 0.15$ and the system becomes metallic between $x \sim 0.35$ and $x \sim 0.40$ (2–5).

The evolution of the resistivity in $Y_{1-x}Ca_xTiO_3$ in dependence of doping x and temperature T is shown in Figure 1a, with the insulating and metallic phases respectively at low and high x. In the IMT region of approximately 0.35 < x < 0.40, resistivity changes of up to five orders of magnitude with x and T can be observed. Furthermore, at x = 0.37, an unusual IMT takes place: Starting off in the metallic phase at low temperatures, Y_{1-x}Ca_xTiO₃ turns insulating across a very large temperature range between approximately 50 K and 170 K. Across the entire temperature range, a hysteresis in the resistivity curve is present (3, 5-10), showing the first-order nature of the phase transition (11) accompanied by phase separation (5, 6, 12, 13). In contrast, the IMT in other well-known correlated systems, like VO₂ (14) or magnetite (Fe₃O₄) (15) proceeds from a low-temperature insulating phase to a high-temperature metallic phase.

In addition to this change in transport properties, a complex variation of the crystal structure takes place across a large range of temperatures and doping concentrations. Upon cooling $Y_{1-x}Ca_xTiO_3$ (0.37 $\leq x \leq 0.39$) from room temperature, the crystal structure changes from a high-temperature orthorhombic (HTO) structure of *Pbnm* symmetry to a monoclinic one (low-temperature monoclinic, LTM) of $P2_1/n$ symmetry

around 230 K (6), i.e. at temperatures above the IMT. Both of these phases are of insulating character (6). In the LTM phase, assuming a doping of approximately $x \approx 0.5$, Ti³⁺ and Ti⁴⁺ atoms order in a threedimensional checkerboard pattern (9, 10), as shown in Figure 1b. Forbidden reflections along (0kl) with odd k, which are usually forbidden for this symmetry, become allowed due to this charge ordering. As a consequence, the (011) reflection is a specific probe for the ordered LTM phase (9, 10, 16, 17). A second crystallographic transition coincides with the IMT: A low-temperature orthorhombic (LTO) phase forms and starts to coexist with the monoclinic phase. The LTO phase has been associated with a metallic character (6), potentially arising from a shorter unit cell axis b which causes strain (6, 12). The temperature of this second, combined phase



Figure 1: **Properties of** $Y_{1-x}Ca_xTiO_3$. Panel a: Resistivity phase diagram of $Y_{1-x}Ca_xTiO_3$. Data from (9, 10). Panel b: Crystal structure ($P2_1/n$) showing a 50-50 distribution of Ti^{3+} (blue) and Ti^{4+} (green) ions, as well as the (011) lattice plane (grey). Panel c: Photograph of the sample crystal. For the measurements, it was oriented such that the $[0k\bar{l}]$ direction was oriented in the vertical and the [h00] direction was aligned in the horizontal plane. Principal crystallographic directions a, b, and c are indicated by red, green and blue arrows in panels b and c.

transition depends on the doping *x*, and was found to be 60 K for x = 0.37 and 140 K for x = 0.39 (6). The two low-temperature phases form a phase separated state, with the volume fraction of the LTM phase decreasing with temperature, until a fraction of about 20% (x = 0.39) to 80% (x = 0.37) remains at 20 K (6).

Phase separation (18-20), is a known phenomenon in a range of quantum materials, like the cuprates (21-24), pnictides (25, 26), manganites (27) and vanadium oxides (28–30). In $Y_{1-x}Ca_xTiO_3$ with doping levels between 0.35 and 0.40, phase separation has been described theoretically (11, 31) and observed experimentally with transmission electron microscopy optical and photoemission microscopy (12),measurements (13) and soft X-ray absorption spectroscopy, supported by density-function theory calculations (5). The domains were observed to be pinned, coexist across the entire temperature range from 10 K to room temperature and are associated with the LTO and LTM phases (13). The shape and size of the different crystallographic domains differs for orientations, but was previously found to be in the range of $1 \mu m$ (12) to $100 \mu m$ (13). The question whether chemical inhomogeneity is the cause for the observed domain pattern, leading to spatially varying physical properties like the metal-to-insulator transition temperature- although speculated about (5, 13) remains so far unresolved to our best knowledge.

Here, we present results studying the temperaturedependent phase separation in $Y_{0.63}Ca_{0.37}TiO_3$ by means of soft X-ray full-field Bragg diffraction imaging observing the (011) scattering signal of the LTM phase. The material shows pinned, millimeter-scale stripe domains across the entire sample. The temperature of the X-ray diffraction (XRD) intensity maximum changes drastically on both millimeter and micrometer length scales. By means of energy dispersive X-ray spectroscopy (EDX) and electron backscattering (EBS) measurements performed in a scanning electron microscope (SEM), we find chemical inhomogeneity in the form of a significantly varying calcium concentration x (and an accordingly varying yttrium concentration 1-x) to be the cause for our observations.

2 Experimental

The soft X-ray diffraction (XRD) measurements were performed at beamline P04 (32) of the synchrotron source PETRA III located at DESY in Hamburg, Germany. A rhodium coated monochromator grating with a line density of 1200 mm^{-1} was used to transmit X-rays with an energy of $1824 \text{ eV} \pm xy \text{ eV}$ to the Kirkpatrick-Baez (KB) focusing mirrors. The exit slit of the monochromator was deliberately opened to a width of 2.2 mm. Using the KB mirrors, the beam was focused in the vertical direction (dispersion direction of the monochromator) resulting in a vertical spot size of approximately 0.7 mm due to the open exit slit. In the non-dispersive horizontal direction, the beam was only slightly focused to a size of approximately 1.4 mm.

As a sample environment, we used an ultrahigh vacuum diffractometer similar to the MUSIX endstation (33-35). The sample was a Y_{0.63}Ca_{0.37}TiO₃ single crystal. The sample, which was fabricated by a floating-zone melting technique (9, 10), was mounted on a cryostat and cooled within a temperature range between 30 K and 300 K using liquid helium. Since the cryostat is rather long in vertical direction, even minor temperature changes result in a noticeable sample movement along the vertical direction, which was corrected for during the data analysis. X-ray diffraction (XRD) of the (011) plane was recorded at an incidence angle θ of 52.1° (with respect to the sample surface) and a scattering angle 2θ of 104.2°. The sample with the (011) surface cut was oriented such that the $[0k\bar{l}]$ direction pointed upwards and the [h00] was oriented in the horizontal plane, as shown in Figure 1c.

An off-axis transmission Fresnel zone plate (FZP) was used to image the diffraction from the 1 mm² X-ray spot on the sample onto a two-dimensional charge-coupled device (CCD). The opaque zones of the FZP consists of silicon oxide structures on a silicon nitride membrane, fabricated by electron beam lithography (*36*, *37*). The outer radius measured 2.15 mm. The aperture of the zone plate was 2 mm by 2 mm, and its focal length at a photon energy of 1824 eV is 158 mm. The sample-zone plate and zone plate-detector distances were 171 mm and 2163 mm, respectively. Correspondingly, a magnification of approximately 13 enabled us to realize a spatial resolution better than 2 μ m, as we have previously shown with a similar setup (*38*) for soft Xray absorption.

The CCD detector (model Andor iKon M) had a chip size of 1024 by 1024 pixel and a pixel size of 13 μ m.

The high flux delivered by the synchrotron source PETRA III and transmitted by the beamline P04, as well as the open exit slit, resulted in a photon flux of approximately $3 \cdot 10^{14}$ photons per second on the sample. This allowed us to use short exposure times of only one to three seconds for images of the Bragg diffraction from the entire illuminated area of approximately 1 mm^2 . In order to study the domain distribution in Y_{0.63}Ca_{0.37}TiO₃, two different scanning procedures were used: (i) Two-dimensional scans of the entire sample, measuring 4 mm (vertical) by 2.5 mm



Orthorhombic

Monoclinc

Figure 2: **Stripe domains in Y**_{0.63}**Ca**_{0.37}**TiO**₃. Panel a: XRD intensity map measuring 1 mm × 3 mm (h × v) of the (011) diffraction peak taken at 137 K showing the spatial distribution of the monoclinic phase. The inset shows an image of the sample crystal with the regions of panel a (black rectangle) and panels shown in b and c (white square) marked. Panels b and c: Small region of interest (ROI, marked in a with a white square) of $300 \times 300 \ \mu$ m² for temperatures between 97 K and 176 K during a heating (b) and cooling (c) cycle. The XRD intensity of the data recorded at 176 K was multiplied by a factor of 2. White scale bars measure 100 μ m.

(horizontal) were performed employing 100 μ m steps with an exposure time of 3 s at temperatures between 97 K and 196 K during both a heating and a cooling cycle. At the start of the heating cycle, the sample was cooled to 45 K, and at the start of the cooling cycle, the sample was heated to room temperature. Before data at a newly set temperature was taken, the sample was given 1 h for equilibration. During data acquisition, the sample temperature was kept stable to a precision of \pm 1 K. The results of this acquisition scheme are shown in Figure 2. (ii) To obtain a more detailed picture of the temperature dependent evolution of different regions in the sample, a dynamic scanning procedure was used to drive a heating and cooling cycle starting from 65 K to room temperature and back to 35 K. While the sample temperature was changing, quick scans of the vertical sample position were performed, scanning a range of 4 mm in steps of 100 μ m with an exposure time of 1 s.

A scanning electron microscope was used to perform energy dispersive X-ray spectroscopy measurements. Line scans across a distance of 50 μ m were measured for acceleration voltages of 10 kV, 20 kV and 30 kV. Furthermore, a two-dimensional raster scan of an area of 50 μ m \times 50 μ m with a step size of 250 nm. Measurements of backscattered and secondary electrons were performed at an acceleration voltage of 30 kV.

3 Results

Figure 2a shows the distribution of areas with significant contributions of the low-temperature monoclinic (LTM) phase across a large region of the Y_{0.63}Ca_{0.37}TiO₃ sample, measuring 1 mm by 3 mm at 137 K. As discussed in the introduction, XRD at the (011) peak is a selective probe for the LTM phase, so that high-intensity regions directly map the distribution of the LTM phase, whereas low-intensity regions map the high/low-temperature orthorhombic (HTO/LTO) phases (9, 10, 16, 17). An image of the sample crystal, taken with an optical microscope, is shown in the inset with the regions of panels a (black rectangle) and b, c (white square) highlighted. Monoclinic (bright) and orthorhombic (dark) phases coexist in long, curved stripes with generally uniform periodicity oriented approximately in direction of the diagonal from bottom left to top right. A single stripe can be more than a millimeter long. In the region on the bottom right, the LTM stripes are most intense. The temperature evolution of the stripes is shown for a small region of interest (ROI, white square in Figure 2a, measuring 300 µm by 300 µm) in Figure 2b for heating and 2c for cooling of the sample. A common color scale was used for all panels, except the one at 176 K, where all intensities were multiplied by a factor of 2. This temperature series shows, that the stripes are pinned throughout subsequent heating-cooling cycles, which is in line with previous observations of domains in Y_{0.63}Ca_{0.37}TiO₃ (13). At 97 K, the stripes in the bottom right corner are of higher intensity, whereas stripes in the rest of the ROI are darker. As consequence of the hysteresis of the phase transition, the stripes at this temperature are slightly brighter during the cooling cycle. At 117 K and 137 K, the stripes are still visible and of generally similar intensity. Even at 176 K they can still be distinguished, albeit at apparently lower



Figure 3: Mapping of the XRD temperature dependence. Panel a shows the temperature of the maximum XRD intensity during sample heating in the same sample region as shown in Figure 2a and on length scales larger than the stripe periodicity. Temperatures of the maximum XRD intensity on short length scales (for sample heating) is shown in panel 3b (corresponding to the sample region shown in Figure 2b and 2c and as a white square in panel 3a). Panel c shows exemplary temperatureintensity curves for sample heating (dashed line, stronger color) and cooling (full line, more faint color). The variation on long length scales is shown by the lower green and black curves, extracted from the respective positions marked by crosses in panel a. The variation on short length scales is shown by the blue and red curves, respectively extracted from the peaks and valleys of 17 neighboring stripe periods taken from the red-blue rectangle and shown for one pair in panel b. The shading shows the one sigma standard deviation of the average and the arrows indicate the direction of temperature change applied to the sample.

intensity. The width and periodicity of the stripes shows a slight dependence on the position on the sample. Especially in the bottom right corner, where the bright stripes are much wider than the narrow stripes. These wide stripes are brighter at 97 K as compared to the thinner stripes, which are brightest around 137 K.

For a more detailed study of the temperature evolution of the phases in $Y_{0.63}Ca_{0.37}TiO_3$, we used the dynamic temperature scanning approach, described in the experimental section, yielding a temperature-dependent XRD intensity trace for the same ROIs as shown in Figure 2. This data set is shown in Figure 3. It shows how critically the characteristics of the temperatureintensity traces depend on the sample position. Figure 3a evaluates length scales larger than the \sim 13 µm period of the stripes by averaging XRD signal from regions measuring approximately 20 μ m (h) by 30 μ m (v). The temperature of the XRD intensity maximum varies strongly, ranging from above 160 K in the upper left region down to below 100 K in the lower right region. A similar evaluation for length scales smaller than the stripe periodicity is shown in panel b of Figure 3 where the temperatures of XRD intensity maxima are shown for regions measuring $2 \mu m$ (h) by $3 \mu m$ (v). Here, one can see that even on length scales of the stripe periodicity, drastic changes in the temperature-intensity profile can be observed with changes up to approximately 40 K within a single stripe period. Panel c of Figure 3 shows temperature-intensity curves of a heating-cooling cycle for short and long length scales. The green and black curves, taken from the spots marked by crosses of the respective colors in panel a, show how the temperature dependence of the XRD intensity changes across millimeter length scales. The red and blue curves respectively show the XRD temperature dependence averaged from 17 adjacent peak and valley regions within the red-blue box shown in panel b. Two exemplary regions are shown by the red and blue rectangles.

To gain more information on the origin of the stripe domains in Y_{0.63}Ca_{0.37}TiO₃, we used a scanning electron microscope (SEM) to perform energy dispersive X-ray spectroscopy (EDX) measurements to study the spatial variation of the chemical composition of the sample. According to the intensity variation in element-specific fluorescence line intensities (Y $L\alpha_1$ and Ca $K\alpha_1$), the elemental concentrations can be determined. The results are shown in Figure 4. A two-dimensional raster scan across an area of (50 µm)² shows a periodic, stripe-like variation of the calcium and yttrium concentration, as depicted in panels a and b of Figure 4, respectively. Furthermore, panels c and d in Figure 4 show that backscattered electrons, which are sensitive to the contrast between heavier (yttrium) and lighter (calcium) elements, show the same stripe pattern as observed by XRD (see Figure 4c). In contrast, secondary electron which originate from the sample surface do not show



Figure 4: Chemical inhomogeneity in $Y_{0.63}Ca_{0.37}TiO_3$. The variation in calcium and yttrium content, as inferred from EDX measurements, is shown in panels a and b, respectively, displaying the same stripe structure as observed in the XRD (c) and electron backscattering data (d). The white rectangle in c and d shows the region of panels a and b. Panel e: Comparison of a line scan of calcium (blue) and yttrium (green) content compared to the XRD data (red). Line scans were measured along the upper edge of the white square shown in c and d.

the stripe pattern, leading to the conclusion that it is only present in bulk regions. A comparison of a lineout of the XRD data and an EDX line scan (Figure 4e) shows that the variation in the Ca and Y concentrations is respectively directly and reversely related to the measured diffraction intensity.

To summarizes these results, we observe stripe domains originating from a separation of LTM and LTO/HTO phases with an average periodicity of about 13 µm and a length up to a few millimeters. The LTM-stripes can be observed by XRD across a large temperature range from approximately 40 K to beyond 180 K with the temperature of maximum diffraction intensity strongly varying on both micrometer and millimeter length scales. Because of the high flux and short acquisition times enabled by our full-field XRD measurement scheme, we were able to scan large regions of the sample, showing that the stripes are not linear but curved and a connection to specific crystallographic orientations can thus be ruled out. Throughout subsequent heating and cooling cycles, the stripes are pinned to the same position on the sample. In the following section, we turn to the interpretation of these observations.

4 Discussion

By quantifying the EDX results, we find that the chemical Ca composition varies by about two

percentage points from 36.1% to 38.2% (for an assumed sample-averaged doping of 37%) and the Y composition varies between 61.9% and 63.6% (for an assumed sample-averaged doping of 63%). It was previously speculated, that stripe domains in $Y_{0.63}Ca_{0.37}TiO_3$ may be the result of spatially varying physical properties (*13*) or chemical inhomogeneity (*5*) but to our knowledge this data provides experimental proof for varying chemical inhomogeneity in $Y_{0.63}Ca_{0.37}TiO_3$ for the first time.

With these results, we directly relate the stripe pattern measured by XRD with a changing chemical composition in the sample: Regions with increased calcium content (i.e. increased hole-doping) show a stronger monoclinic XRD signal. As described in the introduction, the IMT and also the crystallographic phase diagram of $Y_{1-x}Ca_xTiO_3$ is extremely sensitive to the exact doping in the range of x = (35% - 40%) (see also Figure 1). If, for example, we consider a temperature of 140 K, a doping change of x by two percentage points can change the resistivity by a few orders of magnitude (see Figure 1), or it can change the volume ratio of the LTM phase from 80% to 20% (6, 7, 12). The measured change of approximately $x \pm 1\%$ thus means that the local phase composition in the temperature regime of LTM/LTO coexistence strongly varies. This is corroborated with a detailed look at Figure 3c: The hysteresis of the phase transition that is observed when averaging over the stripes (green and black curves in Figure 3c) looks similar to that observed

in resistivity measurements (3, 5, 6, 9, 10) with the maximum intensity being lower for the heating process and the hysteresis present on the low-temperature slope. Since resistivity measurements provide a of spatially averaged picture, a strong similarity is found, when we spatially average our data. This similarity is instead not retained on short length scales when temperature-intensity profiles are extracted only from peak and valley regions, respectively shown in red and blue. For the peak regions (red), a cross-over of the intensity of the heating and cooling cycle can be observed around 120 K.

Previous observations of domains in Y_{0.63}Ca_{0.37}TiO₃ (12, 13) reported different domain patterns depending on the observed crystallographic direction. Transmission electron microscope measurements (12) found stripes in the (a, b)-plane, pointing along the [100] direction, diamond shapes in the (b, c)-plane, elongated along the [001] direction and round domain boundaries in the (a, c)-plane. By means of optical microscopy, wavy stripes were observed in a (100) surface orientation, cigar-shaped domains in a (010) surface orientation, and islands elongated along the adirection were observed in the (001) surface orientation. This shows that previous work identified that the observed shape of domains changes with observed crystallographic directions. The stripes observed in this experiment were acquired from the (011) reflex and therefore represent a different cut. Furthermore, the fact that we observe the stripes to be curved suggests that there is in fact not a single preferred alignment regarding the crystallographic direction of this singlecrystalline sample. With the current experiment, we cannot conclude on the shape of the stripes in the third dimension. Future studies need to address the question how ubiquitous the observed stripe formation is along other crystallographic directions and also in related materials. Our results, enabled by the full-field x-ray diffraction imaging approach, may provide the for previously observed explanation domain coexistence in $Y_{0.63}Ca_{0.37}TiO_3$ (5, 12, 13) and prove that local chemical variations are responsible for the stripe formation, as was previously speculated (5, 13).

A possible explanation for the curvature of the stripe pattern is that the chemical inhomogeneity is introduced during the sample fabrication process. To fabricate the samples, a floating-zone technique was used, which is routinely applied in the fabrication of titanate samples (1, 7, 9, 39). Both the feed and the seed rod are rotated during the process to avoid formation of striations from Marangoni convection (40). The curvature of the observed stripe pattern approximately in the center of the sample are of elliptical shape with minor and major axes diameters of 5.5 mm and 7.5 mm (in the present cut), which roughly matches the size of the fabricated cylindrical crystal rods (9). Thus, we conclude that the chemical inhomogeneity may originate from the sample fabrication method. To clarify exactly which (combination of) parameters causes the stripe formation requires a systematic study of the observed stripe formation in dependence of varying sample fabrication parameters.

5 Conclusion

In this work, we presented measurements of the insulator-metal and crystallographic phase transition in Y_{0.63}Ca_{0.37}TiO₃ using a full-field x-ray diffraction imaging approach. The exceptionally high soft X-ray flux provided by beamline P04 of the synchrotron radiation source PETRA III combined with our experimental approach that allows us to use a large Xray bandwidth, resulted in a field of view of approximately 1 mm² from which X-ray diffraction data could be recorded within seconds with a spatial resolution of 2 µm. Charge ordering of Ti³⁺ and Ti⁴⁺ sites, occurring in the low-temperature monoclinic phase, allows to selectively probe diffraction only from the (011) reflex of the monoclinic phase, since the diffraction from the same reflex is forbidden for both the high- and low-temperature orthorhombic phases that compete with the monoclinic one. The high throughput of our method enables us to map the entire Y_{0.63}Ca_{0.37}TiO₃ crystal at several temperatures and unidirectional record quick scans for many temperatures.

We observe curved, pinned stripe domains with a period of approximately 13 µm extending across millimeter length scales. These stripes are most prominent in a temperature range between 90 K and 160 K but can still be seen at temperatures down to 40 K in some regions of the sample. By means of energy-dispersive X-ray spectroscopy (EDX) measurements, performed in an SEM, we find proof that the stripes in $Y_{0.63}Ca_{0.37}TiO_3$ are correlated with a periodic change of the yttrium and calcium concentrations of about ±0.01. In this sample, the resistivity behavior and crystallographic phase compositions are sensitive to very small changes. The curved shape of the stripes excludes a purely crystallographic origin for the observed phase separation in the single-crystalline sample and instead suggests external influences as cause, likely occurring during the sample growth with the floating-zone method. To our knowledge, this study provides first experimental proof of the origin of stripe domains in $Y_{0.63}Ca_{0.37}TiO_3$, which are directly related to a varying chemical composition.

Since crystallographic and macroscopic resistivity properties of $Y_{0.63}Ca_{0.37}TiO_3$ are clearly related (see e.g. (6, 13)), the observed stripe pattern may furthermore be the cause for previously observed anisotropic resistivity properties (8). Our observation may explain previous

findings of domains with different shapes along different crystallographic orientations. Future studies on the occurrence and shape of such domains in $Y_{0.63}Ca_{0.37}TiO_3$ along other directions and in related quantum materials will provide a more complete picture of this effect. Nonetheless, we consider our study to present an important step towards a controlled design of macroscopic properties of quantum materials during crystal growth.

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3.3 Zone Plates at FELs for Parallelised Fluence and Delay Measurements

When a pump-probe experiment at an FEL is performed, as described in section 2.2, the full picture of the pump-induced dynamics is often obtained by repeating pumpprobe cycles thousands of times while acquiring statistics and varying the delay and the pump fluence. To pertain comparability, care has to be taken that each acquisition is properly normalized to fluctuations of the stochastic SASE pulses (see Figure 2.5). This can e.g. be done by measuring the incident pulse energies with a gas-monitor detector (GMD) [263, 264]. However, if a monochromator is used downstream of the GMD or third harmonic radiation is used for the experiment, this normalization is not appropriate, necessitating different normalization schemes [8, 119, 265–267]. Furthermore, experimental conditions may not always remain perfectly stable, as the pump laser may fluctuate and the spatial or temporal overlap between pump laser and FEL may change, or the sample may degrade over time because of the continuous irradiation. But also from the perspective of the sample, challenges to the experiment are posed if the sample does not reversibly return to the ground state. Furthermore, if a delay trace is acquired sequentially, jitter and drifts are a limitation to the temporal resolution on femtosecond and picosecond time scales, respectively [268]. This section and Paper IV [4] discuss approaches to mitigate these issues by measuring the delay- and fluence-dependent response of a sample to pump excitation simultaneously and potentially in a single FEL shot.

The X-ray streaking method [269-271] was developed to present a solution by measuring a delay trace of several picoseconds with a single X-ray pulse. In the first version of this technique, a setup was realized which used a split and delay approach based on diffraction gratings [269]. A set of beam splitter transmission gratings divides an incident FEL pulse into a fan of sub-pulses. Each splitting grating creates positive and negative first order diffraction beams, which are used as sets of signal and reference beams. At half the distance to the sample, a second set of recombination gratings is used to direct the beams back onto the sample, forming one spot which is excited by the pump laser, and a second spot which is not pumped for same-shot normalization. Because the beams which propagate successively further away from the optical axis travel longer paths, they are delayed in comparison to the on-axis beam. In that experiment, sets of 15 sub-beams were used to cover a delay range between 19 fs and 1277 fs in 15 discrete steps. Compared to a split-and-delay approach using reflective optics, this method has the advantage that it is stable against mechanical drift and vibrations. On the other hand, general drawbacks are that only a number of discrete delay values are probed and the setup is not very flexible regarding adaptability of the probed delay range. In the soft X-ray range, using this many gratings would result in drastically lowered number of photons on the sample.

Subsequent approaches to the X-ray streaking method used a conceptually simpler approach [270, 271]: An off-axis zone plate was used to focus an incident FEL pulse onto a sample. The parts of the pulse which pass the zone plate closer to the optical axis travel a shorter path in comparison to parts of the pulses which pass the outer part of the off-axis zone plate, essentially reducing the 45 transmission gratings of the previous setup to a single optical element. The negative (defocused) first order was recorded on a separate detector screen for same-shot normalization and to correct for inhomogeneous illumination and diffraction efficiency of the zone plate. The delay range thus recorded in a single shot amounts to approximately 1.5 ps with a discrete step size on the order of 10 fs to 20 fs. The maximum delay range $\Delta t_{\rm max}$ that can be recorded in a single shot with this approach is determined by the number N of illuminated zones and the wavelength λ of the FEL radiation according to:

$$\Delta t_{\rm max} = N^{\lambda/c} \tag{17}$$

In equation 17, c is the speed of light. N is therefore limited on the fabrication side by the minimum structure size which can be fabricated, and on the machine side by the beam size which can be produced [270]. The authors expect that the single-shot delay range could be increased by a factor of about 3 by using different fabrication methods and materials. A further increase would be possible with the use of a reflection zone plate [270]. Since the X-ray streaking technique requires the information on the geometric origin of the different parts of the incident FEL pulse to be retained, it can be applied only to experiments performed in transmission or reflection geometries.

Although both the X-ray streaking setup [269–271] and our time-to-space mapping setup, presented in Paper IV, use off-axis zone plates to record a range of pump-probe delays simultaneously, there are a number of differences: In the X-ray streaking approach, the zone plate is used upstream of the sample and the focus is a small spot that is subsequently illuminated (streaked) by the parts of the FEL pulse diffracted from the different regions of the zone plate. On the other hand, our timeto-space mapping setup uses the zone plate downstream of the sample to image the illuminated area onto the detector. Therefore, our setup can additionally image the fluence distribution in the pump laser focus, enabling one to record a range of pump fluences simultaneously. Moreover, the delay- (and additionally fluence-) dependence can be spatially encoded in different regions of the sample, meaning that large (millimetre-scale) areas of the sample are probed in comparison to the focused spot in the X-ray streaking technique, which makes the latter method more prone to be affected by sample damage that occurs within the single pulse, but less sensitive to sample damage that accumulates over time, if a full delay trace is measured in a single shot. Further implications concern samples which are not homogeneous. With the X-ray streaking setup, inhomogeneities larger than the spot size could be studied by scanning the sample and acquiring single-shot delay traces for every spot. For the time-to-space mapping setup, the implications of inhomogeneities in a sample on data acquisition strategies are detailed in Paper IV and compared to conventional setups. Since our setup images the sample onto the detector, the spatial resolution can be improved in the future by increasing the sample magnification.

Paper IV focuses on the methodological development of the time-to-space mapping setup. Therefore, I want to go into more detail on the physical aspect of the study, discussing why magnetite is a prime example of an IMT material as shown by the experimental results obtained on the laser-induced IMT in the magnetite thin-film.

3.3.1 The Laser-induced Insulator-to-metal Transition in Magnetite (Fe₃O₄)

Magnetite is the first material, in which an IMT was discovered [20, 21]. The abrupt resistivity increase by two orders of magnitude (see Figure 2.2) around 124 K is accompanied by structural changes: The high-temperature metallic phase has a cubic inverse-spinel crystal structure in which Fe³⁺-ions occupy the tetrahedral (A) sites, whereas octahedral (B) sites are occupied by both Fe²⁺ and Fe³⁺ ions [272]. When magnetite transitions to the low-temperature phase, the crystal unit cell doubles to a distorted monoclinic structure [273], characterized by charge and orbital order (COO) [26, 105, 106, 274, 275] within the B-site Fe network. Emerging superstructure reflections can be accessed with resonant X-ray diffraction (RXD) e.g. at the iron $L_{2,3}$ -edges using the (00¹/₂) peak (the notation refers to the high-temperature unit cell) to probe the low-temperature order [105, 106, 181–183]. Accordingly, the reflections vanish in the high-temperature structure.

Figure 3 in Paper IV shows that the COO can be destroyed by IR laser pulses, which is observed by RXD as a rapid, biexponential decrease of diffracted intensity. This has been observed before in magnetite single crystals [140, 141, 184]. The initial reduction of the scattering intensity, which is faster than our experimental resolution of 120 fs, is caused by direct excitation of charge transfer between charge ordered sites [276]. The ensuing picosecond evolution depends on the pump fluence with a previously reported threshold of approximately $1.3 \,\mathrm{mJ \, cm^{-2}}$ at an initial sample temperature of 80 K [141]. As we describe in Paper IV, we do not observe the lowfluence regime because even the lower fluences which we used drive the sample across this threshold (which is actually lower in our experiment because we used an initial temperature of 100 K). At fluences above the threshold, a transient non-equilibrium situation occurs with coexistence of insulating and metallic regions. Within several picoseconds, the volume fraction of the metallic phase grows, and the system evolves towards a homogeneous high-temperature phase. The dynamics of the biexponential decay are characterized by the fluence-dependence of the amplitudes A and B of respectively the fast and slow decay (panels c and d in Figure 3 of Paper IV). The fluence-dependence of the amplitude A of the fast decay behaves differently in our measurements of the magnetite thin-film in comparison to previous results measured on single crystals: Whereas we measure a slope of the linear increase with fluence of $0.08 \text{ rel. u.}/(\text{mJ/cm}^2)$, the previously reported value is $0.3 \text{ rel. u.}/(\text{mJ/cm}^2)$; almost a factor of 4 higher.

As we describe in Paper IV, judging these differences is difficult, because both values were obtained in different experiments at different FELs at different beamlines and there are likely uncertainties arising from differing calibrations of the pump fluences. However, one could speculate whether this observation is rooted in the influence which the substrate has on the thin-film: The presence of the Co_2TiO_4 substrate could influence the initial electron excitation by the IR pulse via strain which stabilizes the ordered low-temperature phase because Co_2TiO_4 has the same inverse spinel crystal structure as magnetite and only a small lattice mismatch of +0.66%. This results for example in the increased transition temperature in these films (127 K) as compared to the bulk (124 K) [102]. The mechanism behind this

stabilization is thought to be tensile strain imposed by the substrate, resulting in increased lattice constants in the film plane. Enlarged inter-atomic distances facilitate the formation of the ordered state, hence an increased transition temperature is observed [102]. As a consequence of this stabilization of the low-temperature ordered phase, the electron transfer from $\mathrm{Fe_B}^{2+}$ to $\mathrm{Fe_B}^{3+}$ sites, which is the process of the initial destruction of the order, may be energetically more expensive. Per incident IR photon, fewer charge transfer excitations could take place leading to a shift of saturation to higher fluences.

However, with the present results, we can not be certain that the observed differences are not simply the consequence of differing experimental conditions. Studying to which extent (if at all) thin-films are different to single crystals would require a dedicated experiment that directly compares both types of sample in conditions that match as closely as possible.

In the following paper⁵, entitled "Simultaneous mapping of the ultrafast time and fluence dependence of the laser-induced insulator-to-metal transition in magnetite", we present the time-to-space mapping method for simultaneous acquisition of relevant delay and fluence ranges in pump-probe experiments at FELs.

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Simultaneous mapping of the ultrafast time and fluence dependence of the laser-induced insulator-to-metal transition in magnetite

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ABSTRACT

Pump-probe methods are a ubiquitous tool in the field of ultrafast dynamic measurements. In recent years, x-ray free-electron laser experiments have gained importance due to their ability to probe with high chemical selectivity and at atomic length scales. Measurements are typically repeated many thousands of times to collect sufficient statistics and vary parameters like delay or fluence, necessitating that initial conditions are restored each time. An alternative is presented by experiments which measure the relevant parameters in a single shot. Here, we present a time-to-space mapping imaging scheme that enables us to record a range of delays and laser fluences in any single shot of the x-ray probe. We demonstrate the use of this scheme by mapping the ultrafast dynamics of the optically induced insulator-to-metal Verwey transition in a magnetite thin film, probed by soft x-ray resonant diffraction. By extrapolating our results toward the conditions found at x-ray free-electron lasers with higher photon energy, we demonstrate that the presented data could be recorded in a single shot.

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I. INTRODUCTION

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The intriguing properties of complex, functional, and quantum materials, like high-temperature superconductivity,^{1,2} colossal magnetoresistance,^{3,4} strange metallic behavior,^{5,6} and insulator-metal phase transitions⁷ have attracted researchers' interest on their quest to engineer and harvest these phenomena for several decades. Excitation with ultrashort laser pulses is a particularly powerful tool to manipulate equilibrium phases or create transient states which do not occur under equilibrium conditions.⁸⁻¹¹ Usually, time-resolved studies are performed using two ultrashort pulses: the first pulse (the pump) starts a dynamic process and the subsequent pulse (the probe) is used to observe the change induced in the sample. Due to typically limited signal levels, this pump-probe process is repeated thousands or millions of times. This allows one to collect sufficient statistics while also varying the temporal separation between the two pulses (the delay) and/or the fluence of the pump pulse.

X-ray free-electron lasers (FELs) offer the opportunity to use x-ray pulses for element-selective and atomic-scale probing with high signal levels and femtosecond temporal resolutions. Many FELs today generate pulses using the process of self-amplified spontaneous emission (SASE),¹²⁻¹⁴ which results in fluctuating pulse properties, like intensity, pulse duration, and spectral content. This characteristic motivated the development of techniques for recording a complete set of information for every single shot. In the post-analysis, the data can then be sorted and binned appropriately. Here, simultaneous detection of a range of parameters offers the opportunity to assign recorded data

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to its respective state, thereby facilitating a study of such systems in the first place. In repeated pump-probe experiments, in general, one needs to take care that each pair of pulses yields the same information. This is compromised, e.g., by fluctuating pump and probe beams or jitter between the two. Furthermore, the sample needs to return to the ground state between the pulse pairs and the pulse energies should not cause permanent damage to the sample. Sometimes though, it is interesting to actually probe nonreversible excitations. In this case or if the sample is destroyed, a new sample or spot on the sample needs to be used for every measurement, posing requirements on the available amount or size of sample. Many of these challenges can be alleviated using approaches that can perform a complete experiment, i.e., measure the required delay (and potentially fluence) dependence, in a single shot.

One possible solution is an experimental setup, which is able to map a range of one or more parameters simultaneously. In the context of x-ray spectroscopy at synchrotrons, this has, for example, been done by mapping a range of incident and emitted photon energies onto an area detector.^{15–17} At FELs, one example of the mapping of pumpprobe delay range is the x-ray streaking method,^{18–20} used at x-ray free-electron lasers to probe a delay range of approximately 1.5 ps in a single measurement. Also different approaches using non-colinear beams^{21–24} have been realized.

Here, we present the results of setup that enables the simultaneous recording of a delay range of seven picoseconds and a relative fluence range of a factor of more than five. We use an x-ray optical Fresnel zone plate to image the iron L_3 -edge resonant soft x-ray diffraction (RSXD) signal from a magnetite sample. A non-collinear pump-probe geometry with an angle of 73.25° between the pump and probe beams allows the pump-probe delay to be mapped onto a spatial axis on the detector (see Fig. 1). The orthogonal axis images the signal across the laser beam spot onto the detector, essentially mapping the



FIG. 1. Time-to-space mapping setup. Soft x-ray pulses from FLASH resonant to the Fe L_3 edge (blue) probe the resonant scattering of Fe₃O₄ upon pumping with 800 nm pulses (red). The horizontal scattering plane is shown in yellow. The incidence and scattering angle θ is 32.75° with respect to the sample surface and the pump laser is incident onto the sample under an angle α of 16° with respect to the sample surface normal. Due to the relative angle between FEL and pump, a delay range of several picoseconds is probed simultaneously. An additional delay Δ_{DS} can be set by a mechanical delay stage. An off-axis Fresnel zone plate images the resonant scattering of the unfocused FEL beam from the sample onto a two-dimensional CCD detector.

pump laser fluence distribution. The concept of mapping a range of fluences by using zone plates have previously been reported.^{25,26} With our setup, a large parameter range can be acquired in a static geometry without scanning. Given a sufficiently high signal, such a setup even allows capturing a complete dataset in a single shot.

As a sample, we chose a thin magnetite (Fe₃O₄) film. Magnetite continues to serve as a model system for how charge, orbital, and lattice degrees of freedom shape an insulator–metal transition, here called Verwey transition:^{27–40} Below 124 K, the resistivity increases by two orders of magnitude due to a structural transition from a high-temperature cubic inverse-spinel structure to a distorted monoclinic structure,⁴¹ characterized by charge and orbital order (COO).^{35,36,38–40} The excitation of the magnetite low-temperature phase with ultrashort infrared (IR) laser pulses destroys the COO superstructure and drives the system into the high-temperature structure within several picoseconds.^{42–47} Previous time-resolved IR pump, RSXD probe studies^{42,43} on magnetite bulk single crystals observed a two-step process on femto- and picosecond time scales, characterized by an initial sub-picosecond reduction of the scattering intensity caused by direct excitation of charge transfer between charge ordered sites.^{33,44}

II. METHODS

As outlined in the Introduction, a non-colinear geometry of FEL and pump laser is realized in our time-to-space mapping setup, schematically sketched in Fig. 1: Due to the angle between the two beams, the relative pulse front arrival time of both pulses varied along the horizontal dimension, thereby mapping a time (i.e., relative delay) axis to the horizontal space coordinate of the sample. With an off-axis Fresnel zone plate (FZP), the resonant diffraction signal from the sample, including this delay axis, was spatially resolved by imaging onto a twodimensional charge coupled device (CCD). The delay range which can be covered in a single shot was determined by the geometry of the experiment (incident angles of FEL and laser beams), as well as the magnification of the FZP and the properties of the detector. In the present setup, the delay axis was mapped on the CCD as 23.6 fs/pixel. In principle, this would allow us to record a delay range of up to 50 ps, but in our experiment, the simultaneously recorded delay range was limited by the horizontal sample size to approximately 7 ps. Like in a conventional pump-probe scheme, the recorded delay range can be further extended by scanning the pump laser delay stage (Δ_{DS} in Fig. 1).

Both the FEL and the probe laser illuminate an extended area on the order of one square millimeter on the sample, necessitating a homogeneous sample with flat high-quality surface is required. Here, a high-quality magnetite thin film was used. In addition to being flat, thin films epitaxially grown on spinel Co_2TiO_4 substrates that closely match the crystal structure and lattice constant of magnetite have been shown to have excellent properties:⁴⁸ The resistance hysteresis width of the Verwey transition matches that of the bulk, the correlation length of the COO is comparable to bulk single crystals, and the Verwey transition temperature even surpasses that of the bulk by 3 K.

In order to keep the laser profile rather homogeneous along the probed horizontal direction, which is used as delay axis, we used a cylindrical lens to focus the optical laser to a horizontal line on the sample. In the vertical direction, the laser is focused much stronger, well below the size of the probing FEL beam, such that the full vertical spatial laser profile was probed simultaneously. In the data analysis, we could, thus, separate regions in the center of the vertical laser spot

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profile, which were pumped with a high local fluence, from more weakly pumped regions further away.

Our imaging setup recorded two spatial dimensions simultaneously. We used our special experimental configuration to map the spatial coordinates onto one temporal and one local fluence axis. As this scheme introduces a correlation of signals recorded with different delays and fluences with sample position, it works best with samples that are spatially homogeneous over the probed area. If dynamics of a non-homogeneous samples are of interest, our setup has the advantage of parallelizing the data acquisition in comparison to a conventional pump-probe scheme. In such a conventional scheme, inhomogeneities would be studied by focusing the FEL to a spot as small as possible (with damage-related limitations to the usable total number of photons). Subsequently, a full dataset would require a four-dimensional scan of pump-probe delay, pump laser fluence, and the two lateral dimensions of the sample. In this case, our setup reduces the required scanned dimensions from four to the two spatial dimensions. The ability to study inhomogeneities is closely tied to the spatial resolution of our setup, which we estimate to be around $3-4 \,\mu\text{m}$ for the present geometry¹⁶ (see also Sec. III). In the present experiment, we scanned the relative pump-probe delay Δ_{DS} (see Fig. 1) back and forth by 3 ps using a movable delay stage, thereby moving the entire 7 ps delay window horizontally over the sample surface. This scan also served as a cross-calibration of the delay axis (see below and Fig. 2).

III. EXPERIMENTAL SETUP

Measurements with the time-to-space mapping setup were performed at beamline BL2^{49–51} of the free-electron laser (FEL) FLASH at DESY in Hamburg, Germany, using the ultrahigh-vacuum diffractometer MUSIX.⁵² The schematic experimental setup is shown in Fig. 1. To record resonant diffraction from a magnetite sample at the iron L_3 -edge at FLASH, third harmonic radiation with a central photon energy of 706 eV was used. The full width at half-maximum (FWHM) bandwidth of the FEL pulses was approximately 3.6 eV. The pulse



FIG. 2. Pump-probe data treatment. The pump-probe delay varies along the horizontal x axis because of the different incidence angles of FEL and pump laser. Panels (a) and (b): Normalized images of the pump effect on the sample obtained by dividing pumped by unpumped events for delay stage position ranges of $\Delta_{DS} = (0 \pm 0.5)$ and $\Delta_{DS} = (2 \pm 0.5)$ ps, respectively. One positional unit on the detector corresponds to 13.5 μ m. Panel (c) shows the laser beam profile (green, upper axis) and the corresponding profile of the diffracted signal (cyan, lower axis), obtained by averaging only the pumped signal in panel (b) along the horizontal axis. Panel (d): By scanning the pump laser delay stage position Δ_{DS} (see also Fig. 1) and plotting the average of detector *y* positions pumped with the highest fluences against the delay stage position [data shown along the red lines are extracted from panels (a) and (b)] allows one to observe how temporal overlap moves along *x* (black dashed line). The slope of the black dashed line can be used to translate every row onto a common delay axis. The x axis and y axis have been binned by a factor of 8 and 6, respectively. Panel (e) then shows the dataset on the common horizontal delay axis, while the vertical axis still shows the mechanical delay stage position. Pump-probe traces, as shown in Fig. 3, are finally derived by averaging the data in panel (e) along the vertical dimension.

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energy of the FEL fundamental was on average 20 μJ and the third harmonic emission is usually two to three orders of magnitude weaker. $^{53-55}$

The unfocused FEL beam had a diameter of approximately 4.2 mm at the sample position. The pump laser⁵⁶ wavelength was centered around 800 nm, the pulse duration was 57 fs FWHM, and the pulse energy was 16.8 μ J. The combined temporal resolution of the experiment was ~ 120 fs (see the supplementary material).⁶¹ The laser spot measured approximately 2.6 mm (horizontal, FWHM) by 0.2 mm (vertical, FWHM) and was focused such that a flat-top region formed in the horizontal direction (see the supplementary material, Fig. S1).⁶¹ The sample was horizontally smaller than the laser footprint, extending only in the flat-top region of the laser focus. The pulse repetition rate of the FEL was 10 Hz, while that of the pump laser was 5 Hz so every other FEL shot probed the unpumped sample, serving as a reference for normalization of the signal. We verified that the sample was fully recovered in between shots. Due to the small third harmonic fraction of the FEL beam, the scattering cross section of the sample and the large FEL footprint, the count rate for the dataset was on average 0.54 counts/shot. In total, the data shown here comprises 12 h of acquisition time and approximately 230 000 counts.

The pump laser beam was incident under an angle of 16° with respect to the sample surface normal (see Fig. 1). The sample was a 40 nm thin magnetite (Fe₃O₄) film, grown on Cr₂TiO₄ (001),⁴⁸ measuring approximately 1.9 mm (horizontal) by 8 mm (vertical). The incidence angle θ of the FEL was 32.75° with respect to the sample surface to fulfill the Bragg condition for the (00¹/₂) superstructure peak. The sample was cooled to a base temperature of 100 K for the entire duration of the measurements. An off-axis Fresnel zone plate (FZP) imaged the diffraction signal onto a two-dimensional charge-coupled device (CCD), thereby magnifying the diffraction signal from the sample by a factor of 4.1. Further details on the experimental setup can be found in the supplementary material.⁶¹

IV. RESULTS

As described in Sec. II, we obtained data as a function of the horizontal sample position, x, the vertical sample position, y, and the delay stage position, Δ_{DS} . How we obtain the calibration of the delay axis on the detector coordinates from this multidimensional dataset, as well as data treatment steps used to obtain fluence-dependent delay traces, are visualized in Fig. 2. Small regions of the sample imaged at delay stage positions Δ_{DS} of 0 ± 0.5 and 2 ± 0.5 ps are shown in panels (a) and (b), respectively. In both panels, the depicted pump signal has been normalized to the unpumped signal. The part of the sample where the COO was pumped away by the laser is visible as the blue area. The horizontal position where both pulses cross the surface at the same time (time overlap, t_0) can be seen to be the *x* position where the signal transitions from high to low scattering intensity (black dashed lines). We chose the origin of the Δ_{DS} scale such that t_0 is in the horizontal center of the detector window (x = 150 px) [see Fig. 2(a)].

The vertical profile of the signal which is averaged in the pumped area of panel (b) along the x axis is shown as turquoise data in panel (c) of Fig. 2. This profile maps the local strength of the pump-probe effect and follows the local fluence profile of the laser, which we show overlaid to the pump laser profile as extracted from an independent knife edge scan (green).

We now focus on calibrating the delay scale. For this, we use the region with the largest pump effect in the vertical center of the laser spot profile. We average the *x*-traces with pump fluences higher than

4 mJ/cm² and plot these for the different delay stage positions as a map [Fig. 2(d)]. t_0 extends along a diagonal (dashed line) reflecting the linear influences of both x and Δ_{DS} on the delay. The slope of this diagonal line yields the delay mapping factor on our detector (here 23.6 fs/px). This value depends on the relative incidence angle between FEL and pump laser, the sample and observation angles, the magnification of the imaging zone plate, and the pixel size of the detector. By choosing these parameters, the setup-limited temporal resolution can be tuned to match the experimental requirements.

With this conversion, we can align each row to a common delay axis [see Fig. 2(e)]. A common delay trace using all available data are then obtained by averaging the data in Fig. 2(e) along the *y* axis. We note that there is a hint toward a small sample position dependence of the observed pump effect; it appears that the sample region that is mapped onto $x \approx 90$ exhibits a somewhat slower pump dynamics, which can be seen as a comparatively higher intensity around a delay value of 1 ps for delay stage positions of approximately 2.5 ps. However, the present dataset does not have sufficient quality to study this rather weak effect in more detail.

Usually, the pump-fluence dependence of the ultrafast response of the sample to IR excitation is determined by repeating the pumpprobe experiment with different pump laser attenuation settings. In our setup, we can do this by sorting different rows of the detector image according to the pump fluence at that position [see Fig. 2(c)]. We chose to sort the data into five fluence bins (see the supplementary material; Fig. S2).⁶¹ Thus, we obtain five delay traces spanning a fluence range between 0.7 and 4.1 mJ/cm² without actually changing the incident laser pulse energy. The resulting fluence-dependent IR pump and RSXD probe traces are depicted in Fig. 3(a), showing a double exponential decay characterized by a fast and a slow component.

The resulting traces were fitted using a double exponential decay function (solid lines) convolved with a Gaussian of a width corresponding to the temporal resolution of the experiment (120 fs FWHM) as a fit model. The shaded regions in Fig. 3(a) show the experimental one-sigma standard deviation calculated for each data point during the averaging of multiple traces and binning on the x axis. During the weighted least squares fitting, the inverse experimental error is used as weights for the respective data points. We find that following the IR excitation, a fast and a slow decay process, respectively, named A and B, occur, matching what has previously been observed for single crystals.^{42,43,57} Within our experimental uncertainty, there are no indications of a recovery in the measured delay range.

In panels (b)–(e) of Fig. 3, the fluence dependence of the fit results for the slow decay time constant τ_B (b), the amplitudes A (c) and B (d) and the total long-time decrease A + B (e) are shown. Error bars represent the one-sigma standard deviations. The fast decay is limited by the temporal resolution of the experiment to 120 fs. In the fitting procedure, this is realized by the convolution with the resolution-limited Gaussian function; therefore, the value of τ_A was fixed to a value of 10 fs, much faster than the temporal resolution. Both amplitudes, A and B, show a linear increase with fluence [black dashed lines in Figs. 3(b) and 3(c)]. The slow decay time constant τ_B ranges from 1 to 2 ps, generally matching previously reported values.⁴³ See the supplementary material for more details on the fitting procedure.⁶¹

V. DISCUSSION

In the data shown before, we analyze the temporal evolution of the intensity of the $(00^{1}/_{2})$ superstructure peak, which is a direct

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FIG. 3. Ultrafast fluence-dependent response of a 40 nm thin magnetite film to 800 nm laser excitation. Panel (a): The intensity of the (001/2) superstructure peak decreases on a few-picosecond timescale upon irradiation with the pump laser for fluences between 0.7 and 4.1 mJ/cm². The data were normalized to 1 for negative delays and fit curves were offset by 0.5 relative units (rel. u.) for clarity, and the dashed lines to the right show 0 intensity for the data of the respective fluence. The shaded area is the one-sigma measurement uncertainty of the data, calculated as the standard deviation for each delay value upon averaging several traces of similar fluence and binning on the delay axis. Full lines show fits with a double exponential decay convolved with a Gaussian profile with a width corresponding to the experimental resolution, shown below in black at a delay of 0 ps. The fast time constant τ_A is set to be much faster than the temporal resolution. The fluence dependence of the slower time constant τ_B is shown in panel (b). Panels (c) and (d): Fluence dependence of the amplitudes A (fast process) and B (slow process) alongside linear trend lines with slopes 0.08 and 0.16 rel. u./(mJ/cm²), respectively. Panel (e): The total decay amplitude (i.e., sum of A and B). See the supplementary mater for details on the fitting procedure.

measure for the degree of charge and orbital order in magnetite. In the low-temperature ordered phase, this reflection appears in resonant soft x-ray diffraction (RSXD), e.g., at the iron $L_{2,3}$ -edges and disappears when the sample transforms into the high-temperature phase, indicating the disappearing charge and orbital order.²⁵ The IR pump laser can drive this phase transition and, thus, the $(00^{1}/_{2})$ reflection vanishes as a function of pump-probe delay. The IR pump and RSXD probe results obtained on magnetite thin films qualitatively match those previously reported for single crystals:42,43,57 we find a biexponential decay with a fast time constant τ_A limited by the 120 fs temporal resolution and a slow time constant on the picosecond scale. The linear fluence dependence of amplitude A, previously reported for single crystals,⁴³ is confirmed by our measurements. Quantitative differences beyond these generally agreeing results are attributed to differing experimental conditions: The fact that we do not observe two distinct fluence regimes is because the lowest fluence shown in Fig. 3(a) is already sufficient to drive the sample from its initial temperature of 100 K through the Verwey transition at 124 K. With a higher signal level, our results could have been binned finer to allow drawing conclusions also on the lower fluence regime. Furthermore, the fluence dependence of the fast decay amplitude *A* has been reported to scale as 0.3 rel.u./(mJ/cm²) for single crystals,⁴³ while we find 0.08 rel.u./(mJ/cm²) for the thin-films studied here.

This dependency likely arises because a comparison of fluences in different experiments is challenging. Small deviations coming from differing calibrations in spot sizes and laser pulse energies, different estimates of sample reflectivity (that also relate to surface quality) as well as using different incidence angles and polarizations may add up to sizeable differences. For a quantitative comparison, one would ideally study both sample types in the same setup. As intrinsic sample properties are concerned, differences between our magnetite thin film and a bulk magnetite crystal are expected to be small: A study directly comparing static RSXD and x-ray absorption data of thin films and bulk single crystals only finds minor spectral differences.⁵⁸ The limited film thickness is likely to not explain this behavior, since the x-ray probing depth of around 10-40 nm (Refs. 42 and 43) is shorter than the film thickness. Different thermal conductivities of the film substrate as compared to the bulk sample are expected to influence the evolution only on longer timescales than studied here.

Having discussed the observed dynamics in magnetite, we now turn to our time-to-space mapping method. In its current implementation, signal levels of the setup were limited to approximately 0.5 counts/shot on average. Within an acquisition time of 12 h, we collected about 230 000 shots from the FEL, comprising the data shown in Fig. 3. Mainly two aspects contribute to this rather low count rate: The used pulses from FLASH had 20 μ J pulse energy in the fundamental with an expected contribution at the Fe L-edge of about 20 nJ. Additionally, focusing the FEL beam to a round spot with about 4.2 mm diameter results in a loss of photons of more than one order of magnitude, if compared to the actually relevant photons probing the pumped area of the sample which measured $2 \times 0.2 \text{ mm}^2$. Improving these two aspects could, thus, gain a more than four orders of magnitude in signal. If additionally higher-energy FELs, like the European XFEL, PALFEL, SwissFEL, or LCLS, which can typically produce mJ level pulse energies at these photon energies,⁵⁹ were used, a total gain of about six orders of magnitude could be realized in an optimized experiment. With these improvements, the signal level of a single shot has the potential to substantially surpass that of the full dataset presented here meaning that, our setup can be used in the future to record full datasets on laser-induced dynamics of sensitive samples in a single shot with complete information on time- and fluence dependences.

We note though that the conditions described above result in probe fluences of about 500 mJ/cm², which is certainly beyond the damage threshold of the majority of solids. Consequently, single-shot acquisition becomes a necessity in a measure-before-destroy approach. In order to reduce the probe fluence to a level of <1 mJ/cm², which should be tolerable and non-disturbing to most samples,⁶⁰ the FEL pulse could be attenuated by about one order of magnitude while still yielding a dataset of comparable quality to that shown here. The remaining about two orders of magnitude can be recovered by increasing the probe spot size, for example, by using an FEL spot size of $6 \times 6 \text{ mm}^2$. While solid samples and sample holders of this size are

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not uncommon, this size requirement may pose a challenge if e.g., homogeneous magnetic fields are required to prepare certain sample states. An x-ray focus of this size is routinely achievable with bendable KB-optics which are relatively common at modern FEL facilities. Consequently, the spot size of the optical pump laser would need to be increased accordingly, necessitating an increase in pulse energy to adequately excite the sample.

If these requirements can be fulfilled, the current delay and fluence ranges which are probed simultaneously can be increased. In its current implementation, the setup probes a delay range of 7 ps and a fluence range of more than a factor of five in a single acquisition. The delay range depends on the size of the horizontal pump laser-FEL overlap and the angle between the two. An overlap range of 6 mm, as discussed above, would increase the observed delay range to 21 ps. The current distribution of fluence bins (see Fig. 3 and the supplementary material⁶¹) is currently restricted by the limited signal level. Improvements in signal would enable a finer binning of the laser fluence profile and also allow to increase the probed fluence range to lower fluences.

VI. CONCLUSION AND OUTLOOK

In this study, we present results of a time-to-space mapping setup for time-resolved pump-probe experiments. With this setup, the ultrafast phase transition dynamics of high-quality magnetite (Fe₃O₄) thin films was investigated, induced by 800 nm laser pulses using resonant soft x-ray diffraction at the iron L_3 -edge as probe. The induced dynamics generally match those previously observed in single crystals.

This setup is capable of recording a range of delays (dependent on the dimensions of the sample and the laser and FEL beams) and fluences in a static setup, without the need for any scans. This is achieved within a range of a few millimeters on the sample where the pump laser and FEL overlap, both incident under a relative angle of 73.25°. Due to this angle, the relative delay of both pulses is imprinted into the horizontal dimension on the sample and imaged onto the detector with a Fresnel zone plate. In the vertical direction, imaging the laser spot profile allows for the simultaneous probing of regions of the sample that have been pumped by higher (in the center of the spot) or lower (at the edges of the spot) fluences.

In addition to its use for resonant scattering experiments, the method presented in this work for mapping of delay and fluence ranges can be transferred to other x-ray spectroscopy schemes, like non-resonant scattering, x-ray absorption measured in transmission or reflectivity, and potentially x-ray magnetic circular dichroism. The resonant diffraction efficiency of magnetite at the iron L_3 -edge is about 10^{-4} ,⁵⁷ which is small in comparison to e.g., absorption measured in transmission. Since the necessary sample and spot sizes as well as pulse energies critically depend on the signal level, other detection modalities will change the feasibility of this approach (see Sec. V).

Acquisition schemes similar to our method could also be realized in laboratory-based experiments using high-harmonic generation (HHG). While such a source would not provide enough photons for single-shot acquisitions, the stability together with our non-scanning approach may yield excellent data quality after averaging.

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AUTHOR DECLARATIONS Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

J. O. Schunck: Formal Analysis (lead), Investigation (equal), Visualization (lead), Writing/Original Draft Preparation (equal), Writing/Review & Editing (lead). P. S. Miedema: Investigation (equal), Writing/Review & Editing (equal). R. Y. Engel: Formal Analysis (supporting), Investigation (equal), Writing/Review & Editing (equal). S. Dziarzhytski: Investigation (equal), Writing/Review & Editing (equal). G. Brenner: Investigation (equal), Writing/Review & Editing (equal). N. Ekanayake: Investigation (equal), Resources (equal), Writing/Review & Editing (equal). C.-F. Chang: Resources (equal), Writing/Review & Editing (equal). P. Bougiatioti: Investigation (equal), Writing/Review & Editing (equal). F. Döring: Resources (equal), Writing/Review & Editing (equal). B. Rösner: Investigation (equal), Resources (equal), Writing/Review & Editing (equal). C. David: Resources (equal), Writing/Review & Editing (equal). C. Schüßler-Langeheine: Conceptualization (equal), Investigation (equal), Writing/Original Draft Preparation (equal), Writing/Review & Editing (equal). M. Beye: Conceptualization (lead), Funding Acquisition (lead), Investigation (equal), Project Administration (lead), Supervision (lead), Writing/ Original Draft Preparation (equal), Writing/Review & Editing (equal).

DATA AVAILABILITY

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

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- ⁶¹See the supplementary material for some more detailed information on the calibration of the pump laser fluences, experimental parameters (temporal resolution of the setup, Fresnel zone plate optic, and detector), and the fitting procedure of the pump-probe delay traces.

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Supplementary material for

Simultaneous mapping of the ultrafast time and fluence dependence of the laser-induced insulator-to-metal transition in magnetite

1 Fluence calibration and binning

To determine the pump laser profile, horizontal and vertical knife edge scans through the laser beam were recorded with a diode. The horizontal and vertical laser spot profiles were calculated from the knife edge scans by smoothing the knife edge data with a gaussian filter (sigma of 0.2 mm and 0.02 mm for horizontal and vertical directions) and subsequent derivation (see green line plots in Figure S1). The two-dimensional laser spot was then approximated as outer product of these profiles (see color map in Figure S1). By normalizing the area under the two-dimensional spot to the measured pulse energy of 16.8 μ J, and dividing by the pixel size (13.5 μ m²), the fluence at the position of every pixel in the X-ray measurements is derived.



Figure S1: **Approximation of laser spot** modeled as outer product of a horizontal and vertical knife edge scan. Horizontally, the sample is smaller than the laser spot. The line profiles are cuts along the green dotted lines and were derived by calculating the derivative of the knife edge scans

For the data analysis, it was important to calculate the fluence of each row in Figure 2(a) and 2(b). To achieve this, the vertical fluence profile derived above was compared to the pump effect measured on the sample, shown in Figure 2(c) of the main manuscript. The upper panel of Figure S2 shows a map of the sample (only pumped FEL shots) with the assigned fluence values. Traces with similar fluences were binned as shown in the lower panel of Figure S2 resulting in the traces shown in Figure 3(a) of the main manuscript.



Figure S2: Fluence calibration. Top: Map of all pumped events with the *x* position converted to delay. The fluences for each row, derived as described in the text, are shown next to the data. Bottom: The same fluence values are shown along with bin edges and bin centers that were used for further analysis and fitting (Figure 3).

2 Experimental Methods

2.1 Temporal resolution

The temporal resolution of the experiment was estimated as follows: The electron bunch duration was measured to be approximately 120 fs (FWHM) and the photon pulse duration of the fundamental is expected to be shorter by a factor of about 0.5 to 1, for low and high bunch charges, respectively (1, 2). The used bunch charge of 270 pC is in the intermediate regime. Therefore, an FEL pulse duration of 90 fs (FWHM) is a reasonable, conservative estimate. The third harmonic pulse duration is expected to be similar (3). The temporal resolution τ of the experiment consists of contributions from the FEL and pump laser pulse duration (57 fs as measured with an auto correlator (4)), their arrival time jitter (with respect to the master timing oscillator) and remaining contribution from other sources (5), according to the following equation: $\tau^2 = \tau_{FEL}^2 + \tau_{IR}^2 + \tau_{FEL jitter}^2 + \tau_{IR}^2 + \tau_{other}^2$. A bunch arrival time monitor (BAM) (6–9) was used to measure and correct for the arrival time jitter of the FEL pulses, reducing the term $\tau_{FEL jitter}$ to the resolution of the BAM, which is below 10 fs (6, 10). Furthermore, the jitter contribution of the pump laser is conservatively estimated to amount to 25 fs (FWHM) and the jitter from other sources to 27 fs (FWHM) (5). Thus, the total resolution of the experiment is expected to be $\tau = \sqrt{90^2 + 57^2 + 10^2 + 25^2 + 27^2}$ fs ≈ 120 fs.

2.2 Setup optics – Fresnel zone plate

The Fresnel zone plate (FZP) consisted of silicon oxide structures on a silicon nitride membrane, fabricated by electron beam lithography (11, 12). The width of the outermost zone was 35 nm. The off-axis zone plate is taken from the outer 3 x 3 mm² of a structure with an outer radius of 5.76 mm. At an energy of 706 eV, the focal length was 229.6 mm. With the FZP located approximately 27 cm from the sample, the magnification of approximately 4.1 could be realized. The transmission of the FZP was

around 10% to 15%. The use of an off-axis zone plate provides a convenient way to separate the sample image from the zero-order signal, which would overlap if a full zone plate was used.

2.3 Detector

The detector was a *PrincetonInstruments PIXIS-XO: 2KB* charge-coupled device (CCD) with a chip size of 2048 pixel in horizonal direction and 512 pixels in vertical direction. The pixel size was $(13.5 \ \mu m)^2$. To obtain a read-out frequency of 10 Hz, a region of interest comprising 76 pixels in vertical direction (perpendicular to delay axis) was read out using a 6-fold pixel binning. No binning was used for the horizontal axis. Because of the low average count rate of about 0.5 counts/shot (see main manuscript), a blob finding algorithm was used to identify single photon counts.

3 Fitting of pump-probe delay traces

The pump-probe traces in Figure 3 of the main manuscript were fitted using a least-squares minimization algorithm provided by the lmfit package for python (13) using the sum of two exponents, multiplied with a Heaviside step function H(t) and convolved with a Gaussian profile G(t) (see Equations (1) - (3) and Table S1).

$$f(t) = \left[H(t) \cdot \left(A \cdot \left[\exp\left(-\frac{t-t_0}{\tau_A}\right) - 1\right] + B \cdot \left[\exp\left(-\frac{t-t_0}{\tau_B}\right) - 1\right]\right) + c\right] \otimes G(t)$$
(1)

$$H(t) = \begin{cases} 0; \text{ if } t < 0\\ 1; \text{ if } t \ge 0 \end{cases}$$
(2)

$$G(t) = \exp\left(-\frac{t^2}{2\sigma^2}\right) \tag{3}$$

Symbol	Parameter	Varied during	value
-		fitting	
Α	amplitude of fast process	Yes	-
$ au_A$	decay time constant of the fast	No	0.01 ps
	process		
t_0	time overlap of FEL and pump laser	No	0 ps
	pulses		
В	amplitude of slow process	Yes	-
$ au_B$	decay time constant of the slow	Yes	-
	process		
С	constant offset	No	1
σ	width of the Gaussian convolution	No	0.0565 ps (= 0.120 ps FWHM)
	function		

Table S1: Parameters of the fitting function.

The Heaviside function (2) warrants that the fit remains at *c* for times t < 0. The convolution with the Gaussian function (3) broadens the double exponential to account for the temporal resolution of the experiment. Before the fitting algorithm was used, t_0 was fixed to approximately the value of the first data point which shows decreased intensity in the delay trace averaged across the three highest fluence traces.

During the fitting process, only the parameters A, B and τ_B were varied, while the other parameters were fixed to values indicated in Table S1. The initial guesses for A, B and τ_B were respectively: 8% of the fluence of the fitted trace, 60% of the difference of the first and last 10 points of the fitted trace, and 1.1 ps. Additionally, A was constrained to be within 20% to 180% of its starting value, B was constrained to be larger than 0 and not larger than 1, and τ_B was constrained to be longer than 0.5 ps and shorter

than 5 ps. Furthermore, weights for each datapoint were passed to the fit function corresponding to the inverse of the error shown in Figure 3.

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4 PAX: High-Energy Resolution RIXS Measured with Electron Spectrometers

The method termed photoelectron spectrometry for the analysis of X-rays (PAX) allows to perform a RIXS experiment in a photoelectron spectrometer endstation. A converter is used to convert the RIXS photons, scattered from the sample, to photoelectrons via the photoemission process (see section 2.5). Most of the information available from RIXS is conserved (except e.g. polarisation) and for the detection of the PAX electrons, the very high energy resolution of state-of-the-art electron spectrometers can be utilized. In section 2.7 current efforts to bring the energy resolution of grating-based soft X-ray RIXS down to and below 10 meV are described. With photoelectron spectrometers, energy resolutions down to and below 1 meV can be achieved (see section 2.5.1 and [73, 74, 167–173]). The PAX efforts described in this chapter aim to bring the energy resolution of photoelectron spectrometers to RIXS.

Historically, the PAX method was first realized by Krause to measure binding energies and line widths of fluorescence emission lines 50 to 60 years ago [277– 279] using gases for the conversion of X-rays to photoelectrons. A few years later, a comparison of a solid gold converter to gaseous converters lead to the realization that a solid potentially allows for higher count rates at the cost of a larger background (arising from inelastically scattered electrons) [280]. More recently, a team around Georgi Dakovski at the free-electron laser LCLS realized that the PAX method may present a way to circumvent sample damage that can arise from a combination of the high peak brightness of FELs and the small foci typically used in time-resolved RIXS experiments [281]. In PAX, the converter is the source for the electrons which are energy-resolved by the electron spectrometer. This allows one to increase the spot size of the X-ray beam on the sample without degrading the energy resolution. Thus, the achievable resolution in PAX is decoupled from the spot size on the sample.

The overall count rate in recent PAX experiments is on the same order of magnitude compared to grating-based RIXS setups [5, 281]. On the one hand, the PAX setup gains about a factor of 10^4 in RIXS photon collection efficiency because the converter can be placed much closer (several millimetres) to the sample as typically the first optic in a RIXS spectrometer (which additionally has a smaller aperture in one dimension due to grazing incidence angles). On the other hand, this gain in collection efficiency is compensated by a lower spectrometer efficiency of PAX due to a limited conversion efficiency of the converter and transmission of hemispherical analysers that we used for PAX so far [5, 281, 282]. As discussed qualitatively in Paper V [5] and in more detail in section 4.3, a momentum microscope (MM) in combination with a time of flight (ToF) electron spectrometer promises an increase of up to 1000 in the future.

4.1 High-Temperature Superconducting Cuprates

High-temperature superconducting cuprates were first discovered in the late 1980s [29], sparking a surge of research activity that made this class of materials the most widely studied among the strongly correlated electron systems [48]. Until today, cuprates hold the record for the highest critical temperature T_c at 135 K with the exception for other systems that show a higher T_c under high pressure [48]. The cuprates are characterised by a complex phase diagram with several different phases that depends strongly for example on the elemental composition and the hole or electron doping, and ordered phases were found to compete with superconductivity [283]. The elementary excitations in the cuprates dominate the competition of those phases and, as discussed in section 2.7, RIXS is well-suited to study those excitations [42, 62, 283]. The subsequent description of excitations in cuprates follows [179].

The parent compounds of high-temperature superconductors generally classify as Mott insulators (see section 2.1.1) in which the Coulomb repulsion U is the energy separation of the lower (occupied) and upper (unoccupied) Hubbard bands, formed from 3d bands of copper. Additionally, a charge-transfer gap Δ describes excitations from the O-2p band to the upper Hubbard band that is generally smaller than U. According to the classification by Zaanen, Sawatzky and Allen, this makes cuprates charge-transfer insulators [284]. dd-excitations are charge-driven excitations that exist on an energy scale of a few eV and are described by the crystal field splitting of 10Dq and Hund's coupling constant J_H . They are local in nature and therefore generally show only small momentum dependences. If carriers are doped into cuprates, charge excitations below the gap Δ arise as intra-band excitations on an energy scale t of about 0.4 eV.

Below the energies of charge excitations are magnetic excitations with energy scales on the order of the magnetic exchange interaction J of more than 100 meV in cuprates. They overlap with charge excitations in doped cuprates¹. Spin-flip excitations were predicted in 1998 [285] and observed by RIXS in measurements on undoped La₂CuO₄ in 2010 [286]. If cuprates are hole-doped, magnon excitations broaden but their energy position remains the same [287]. In contrast, the dispersive nature of the magnon survives in the over-doped region (where antiferromagnetic order disappears). This phenomenon is described as a paramagnon, where 'para' refers to the fact that the excitation arises from short-range correlations instead of long-range correlations [283]. In electron-doping regime, the magnon spectral weight moves to higher energies and the peak width broadens [288].

Charge order (CO) in cuprates was discovered in 1995 in the La_2CuO_4 family. Doped holes form one-dimensional charge stripes in the CuO_2 plane that separate antiferromagnetic domains. This CO is observed at hole concentrations where the superconducting transition is suppressed. Thus, it is considered to compete with

¹An example how they can be distinguished - e.g. by analysing the polarisation of incident and/or scattered X-rays - was described shortly in section 2.7.2.
the occurrence of the superconducting phase. In 2012, CO was observed by RIXS with the maximum at a momentum transfer $\vec{q} = (-0.31, 0)$ [110]. The chargeorigin of the observed order was confirmed by measurements of the polarization dependence. Later, similar observations were confirmed in a suite of other cuprates $(Br_{1.5}Pb_{0.6}Sr_{1.54}CaCu_2O_{8+\delta}$ [289], HgBa₂CuO_{4+\delta} [290], Bi₂Sr_{2-x}La_xCuO_{6+\delta} [291], Bi₂Sr₂CaCu₂O_{8+\delta} [292], Nd_{2-x}Ce_xCuO₄ [293]), leading to the conclusion that the competition of CO and superconductivity is a universal occurrence. Understanding this competition is important for a better understanding of the mechanism of hightemperature superconductivity in cuprates.

4.2 State-of-the-art of PAX

After the method of PAX had been conceptualized specifically for RIXS [281] and an algorithm for the deconvolution of the PAX spectrum had been developed and demonstrated [282], the evolution of the method towards an approach that can truly complement grating-based high-resolution RIXS commenced with the experiment presented in Paper V [5]. In this paper, we chose the sample $Ba_2Cu_3O_4Cl_2$ (Ba2342) as a benchmark since its crystal structure and RIXS spectrum are closely related to those of high-temperature superconductors [294]. In particular, a magnon excitation in Ba2342 which disperses to a maximum energy of about 300 meV [294] is a test to the achievable energy resolution. The published grating-based Ba2342 RIXS spectra also served as reference for the measured PAX results and the deconvolved RIXS spectra.



Figure 4.1: Comparison of samples holders as used for ARPES and PAX in the ASPHERE III endstation. In the ARPES configuration (a), the foci of the X-rays (purple cross) and the analyser (black circle) coincide on the sample (blue). In contrast, in the PAX geometry (b), the focus of the X-rays is on the sample but the focus of the analyser is on the converter (yellow).

The experimental geometry of the PAX test setup in the ARPES chamber AS-PHERE III [295, 296], located at beamline P04 [229] of PETRAIII, is described in Paper V [5] and shown in Figure 4.1. Figure 4.1a shows the geometry of a con-

ventional ARPES measurement: the foci of the X-rays and the analyser are both on the same location on the sample. However, for PAX measurements, the foci are separated since the analyser is focused on the electron source (converter) and the X-rays are focused on the sample (see Figure 4.1b), meaning that the distance between X-rays and analyser needs to be adapted. Since the focal distance of the used analyser is fixed, the only option is to steer the X-ray beam with the focusing mirrors. In the case of the ASPHERE III chamber, a Kirkpatrick-Baez (KB) mirror pair at the entrance to the sample chamber refocuses the X-rays onto the sample. Moving the focus across large (more than a millimetre) distances is not usually done during photoemission experiments. In addition, also the sample holder needs to be moved several millimetres, as one can see from a comparison of panels a and b in Figure 4.1. Mitigating both these challenges was only possible because of the flexibility provided by the ASPHERE III endstation. In the future, dedicated PAX instrument, described in section 4.3, this is solved by using an extra manipulator for the converter so that it can be moved independently of the sample, as shown in Figure 4.2.

As opposed to the backscattering converter geometry used in previous PAX setups [280–282], we chose to use a transmission geometry because it allows for a compact design of a sample holder that can accommodate the converter very close to the sample (about $3 \,\mathrm{mm}$, see Figure 4.1b). Additionally, a transmission converter also fulfils the role of a filter to prevent primary photoelectrons as well as Auger and secondary electrons emitted from the sample from interfering with the measurement of the PAX photoelectron signal [281]. The PAX signal is expected to be comparatively small because of the low fluorescence yield of about 1% at the Cu L_3 -edge (see Figure 2.7 and [151]), the solid angle fraction covered by the converter of about $20\%^2$ and the limited conversion efficiency of the converter of about 5% [282]. In total, this yields an expected reduction of the PAX signal of 10^{-4} . On the other hand, assuming that every X-ray photon incident on the sample causes the emission of one photoelectron, the number of expected photoelectrons can be estimated by the relative factor of the X-ray penetration depth (about 400 nm [70]) and the electron escape depth (approximately 2 nm, see Figure 2.9) at 930 eV to be 2×10^{-2} , which is a factor of 200 higher than the number of expected PAX electrons. In the backscattering geometry, used in previous PAX experiments [281, 282], such a filter needs to be inserted between sample and converter. Regarding the thickness of the converters, a few considerations are important: Because of the short inelastic mean free path of electrons in a solid that is significantly below 1 nm at X-ray energies of $930 \,\mathrm{eV}$ (see Figure 2.9 and section 2.5), the converting layer needs to face the analyser, and a thickness of more than a few nanometre is not needed. Furthermore, the X-rays need to be able to reach the converting layer to release the PAX photoelectrons. As a compromise between these considerations on the one hand and concerns for stability on the other hand, we used converters that consisted of an approximately 10 nm thin layer of silver or gold on a 200 nm thin substrate. The transmission values for both of these layers at photon energies of 930 eV are about 90% [70] but decrease with decreasing photon energy. Making the converting layer

 $^{^2 \}mathrm{Assuming}$ a mean distance of the converter of 3 mm from the sample and a converter with a diameter of 4 mm.

even thinner may lead to formation of islands and thus a non-homogeneous film.

The implementation of a deconvolution algorithm for PAX is described in [282], and the way it was used in this work is described in Paper V [5] and its supplementary information (see below). Several aspects are important to achieve a high energy resolution in the deconvolved RIXS spectrum: First, for an accurate deconvolution, it is important that the background is well-characterized in an energy range that extends significantly beyond the region of interest in the PAX spectrum. Background arises from inelastically scattered electrons and the analyser transfer function. The latter depends on many measurement and setup parameters, like the energy of the measured electrons, the pass energy and the measurement position relative to analyser, etc. and can result in a somewhat inhomogeneous distribution across the detector. Next, the photoemission spectrum of the converter needs to be known and measured under conditions that resemble the conditions used for the acquisition of the PAX as closely as possible. The photoelectron spectrum itself contains the energy resolution contributions from the beamline, the analyser and the converter. Since these are deconvolved from the PAX spectrum, the resolution of the resulting RIXS spectrum is in principle not limited by these factors and in an ideal world, the energy resolution would in fact be independent of the setup. However, in the real world, the resolution is limited by the number of measured electrons and the resulting noise level of the PAX spectrum [282]. Therefore, the intrinsic width of the photoemission feature of the converter and the conversion efficiency of the photoemission signal pose an important consideration, as discussed in [5, 282]. The lifetime broadening is important since narrower spectral features allow to deconvolve to better energy resolutions [282]. The gold 4f and silver 3dcore-levels were chosen because of their strong core-level excitation efficiencies, resulting in a higher conversion efficiency [282]. Their photoemission line widths are 335 meV [297] and 233 meV [298] (FWHM), respectively. Narrower line widths can generally be found in photoemission features closer to the valence, but come at the cost of a lower conversion efficiency. An interesting candidate is the platinum Fermi edge, because its width is less than $10 \,\mathrm{meV}$, if the converter is cooled to e.g. $20 \,\mathrm{K}$.

We did try to use the Fermi edge of a platinum converter (which has conversion efficiency that is about two orders of magnitude lower in comparison to the core levels of silver or gold). We acquired a PAX spectrum for about 24 h, but during the data analysis it became clear that the PAX spectrum together with the converter photoemission spectrum does not lead to a realistic RIXS deconvolution. The challenge with such low count rates is that one needs to measure a spectrum for several hours before the data quality is good enough to judge if the spectrum actually exhibits expected features. Therefore, an important conclusion from the measurements of our test setup is that the best energy resolution in PAX is promised from a setup that uses narrow converting features, warrants a background that is well-characterized across a large energy range and converter photoemission spectrum and realizes a decent count rate. In the future, PAX measurements using the Fermi edge for conversion will be enabled by the increased efficiency of a dedicated PAX endstation, as mentioned in the introduction to chapter 4 and discussed in more detail in section 4.3. The expected improvement could enable ultra-high-resolution RIXS. In the following paper³, entitled "A compact approach to higher-resolution resonant inelastic x-ray scattering detection using photoelectrons", we present the development of the PAX method towards a new way of performing high-resolution RIXS.

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A compact approach to higher-resolution resonant inelastic x-ray scattering detection using photoelectrons

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Abstract

The detection of inelastically scattered soft x-rays with high energy resolution usually requires large grating spectrometers. Recently, photoelectron spectrometry for analysis of x-rays (PAX) has been rediscovered for modern spectroscopy experiments at synchrotron light sources. By converting scattered photons to electrons and using an electron energy analyser, the energy resolution for resonant inelastic x-ray scattering (RIXS) becomes decoupled from the x-ray spot size and instrument length. In this work, we develop PAX towards high energy resolution using a modern photoemission spectroscopy setup studying $Ba_2Cu_3O_4Cl_2$ at the Cu L_3 -edge. We measure a momentum transfer range of 24% of the first Brillouin zone simultaneously. Our results hint at the observation of a magnon excitation below 100 meV energy transfer and show intensity variations related to the dispersion of *dd*-excitations. With dedicated setups, PAX can complement the best and largest RIXS instruments, while at the same time opening new opportunities to acquire RIXS at a range of momentum transfers simultaneously and combine it with angle-resolved photoemission spectroscopy in a single instrument.

1. Introduction

Resonant inelastic x-ray scattering (RIXS) has become a prime spectroscopic tool for the study of low-energy elementary excitations, including phonons and magnons [1, 2]. Through the use of x-rays, core-hole resonances can be exploited to selectively probe the active site in complex materials [3]. The sufficiently large momentum of x-rays allows mapping the dispersion of collective excitations [4–8]. By exploiting the photon polarization, symmetry properties of excitations can be analysed [1, 9–13].

However, achieving competitive energy resolution to resolve these phenomena at soft x-ray resonances remains challenging and requires special developments in monochromator beamlines and spectrometer instruments with state-of-the-art gratings, stable mechanics and advanced detectors [14–21]. Further resolution improvements are reaching technological limits in many components simultaneously. Current record resolution is achieved with spectrometers so large that they extend into annex buildings of synchrotron experimental halls [16, 17, 20].

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In this work, we realize a different approach to high energy resolution RIXS termed photoelectron spectrometry for the analysis of x-rays (PAX). Competitive energy resolution with good signal levels is achieved in a compact instrument with a clear path for improvements beyond current records. Our setup also offers the advantage of simultaneous detection of a range of momentum transfers. Furthermore, the instrument can be easily adapted to perform angle-resolved photoemission spectroscopy (ARPES) as another very powerful x-ray spectroscopy technique, e.g. for quantum materials research [22–25].

The idea behind PAX is to convert x-ray photons scattered from the sample into photoelectrons, which are subsequently detected using a photoelectron spectrometer. This technique was pioneered more than 50 years ago [26–28] and has recently been rediscovered for the measurement of RIXS [29, 30]. Scattered x-ray photons are converted into photoelectrons in a specially selected material which ideally shows sharp and intense photoemission lines. According to Einstein's formula $E_{kin} = h\nu - E_b - \phi$, the resulting electron kinetic energy E_{kin} is a direct measure of the x-ray energy $h\nu$ as well as the electron binding energy E_b in the converter for a material with a given work function ϕ . The measured electron spectrum (the PAX spectrum) is thus a convolution of the RIXS emission spectrum from the sample and the photoemission spectrum of the converter. Rigorous characterization of the converter spectrum under identical measurement conditions makes it possible to recover the original RIXS spectrum using deconvolution algorithms.

Using experimental chambers designed for x-ray photoelectron spectroscopy (XPS), previous work [29, 30] has identified advantages of PAX over grating spectrometers: PAX is cost-effective, compatible with photoelectron spectroscopy, and the energy resolution is decoupled from the x-ray spot size, making PAX suitable for experiments at high-intensity free-electron lasers, where sample damage at small spot sizes is a severe limitation. In this work, we explore the capability of this technique to achieve high energy resolution for RIXS experiments and to acquire a significant momentum transfer range simultaneously.

2. Concept

The converter material comprises the core component in our approach and therefore needs to be chosen with care: When measured under exactly the same conditions as the PAX spectrum, the converter spectrum contains all resolution-determining terms, and the true RIXS spectrum could in principle be deconvolved to any energy resolution. However, due to noise in the acquired spectra, the sharpest features in the measured converter spectrum determine the effectively achievable energy resolution. The converter spectrum resolution is limited by the lifetime broadening of the observed photoemission lines or temperature broadening when using the Fermi edge for deconvolution, as well as resolution limits in the beamline and electron spectrometer. While it is challenging to identify materials with core-level emission linewidths below 100 meV and high photoemission cross-sections in the soft x-ray range [30, 31], using the Fermi edge of metallic converters can provide energy resolutions limited only by the converter temperature, albeit at rather low signal levels. Remaining resolution limits are then given by the monochromaticity of the incident beam (i.e. the beamline, with records in the range of 10 meV at the Cu L-edge [16, 17, 20]), the energy resolution of the electron analyser (often reaching below 10 meV energy resolution [23, 32–36]) and by the signal-noise-ratio of the measured data [30, 37]. Resonant excitation of a sample with soft x-rays ejects electrons via photoemission processes as well as Auger decays of core excited states. Inelastic scattering as measured by RIXS is a minority process since fluorescence decays of the core excitations are typically less than one per cent in the soft x-ray range [38]. To detect PAX signals, the overwhelming number of electrons emitted directly from the sample need to be blocked, while the emitted photons need to be transmitted to a converter.

In our approach, we integrate the functionalities of blocking direct electrons and converting the RIXS signal into a single, layered thin-film structure consisting of a support material coated with the converter film (here, e.g. several nanometres of Ag and Au). The converter faces the electron analyser. The thickness of the support is chosen such that it provides mechanical stability, blocks the direct electrons and also maximizes x-ray transmission to the converter film. By placing this device within a few millimetres of the sample, the collected solid angle for RIXS photons can be maximized.

Photons emitted from the sample in different directions are converted to electrons at different positions on the converter. By using the transmission mode of the electron analyser, different scattering angles, i.e. different momentum transfers, can be resolved simultaneously. For example, in our test geometry, the converter has a diameter of 4 mm and is placed at a distance of 3 mm from the sample. With this setup, we acquire scattering angles between 122° and 160°.

Below, we present a study of the antiferromagnetic insulator $Ba_2Cu_3O_4Cl_2$ (Ba2342), which is structurally similar to cuprate high-temperature superconductors. The characteristic RIXS spectra of Ba2342 are well-known [39] and show intense and slightly dispersive *dd*-excitation peaks between 1.5 eV and 3 eV energy loss, as well as a dispersive magnon excitation up to approximately 300 meV. Figure 1. Schematic of the PAX setup implemented into a hemispherical electron spectrometer. Incident x-rays (purple) scatter (blue) from the sample and are subsequently converted into photoelectrons (red circles) using a transmission converter consisting of a thin metallic gold or silver layer (yellow). The photoelectron spectra (energy axis *E*) are measured using the transmission mode of a hemispherical electron spectra (energy axis *E*) are measured using the transmission mode of a hemispherical electron spectra (energy axis *E*) are measured using the transmission mode of a hemispherical electron spectrometer that radially disperse selectrons according to their energy. Furthermore, electrons originating from different locations on the converter, corresponding to different scattering angles 29, can be imaged onto the two-dimensional detector, allowing to record of a range of momentum transfers from x-rays to the

3. Experimental setup

High-resolution PAX measurements are performed at the soft x-ray beamline P04 of the synchrotron storage ring PETRA III at DESY using the permanently installed ASPHERE III endstation (see, e.g. [40, 41]), designed for XPS and ARPES studies. The x-ray beam is monochromatized using a 400 l mm⁻¹ grating and an exit slit width varying between 20 μ m and 100 μ m. At the entrance of the experimental chamber, the beam is refocused with Kirkpatrick-Baez mirrors.

The Ba2342 sample, mounted on a special sample holder close to the PAX converter, is kept at approximately 15 K to 20 K (see figure 1). Electrons are analysed in a VG Scienta DA 30 hemispherical analyser. The sample was cleaved in air before insertion into vacuum. The surface was oriented such that the Cu-O planes extended along the sample surface directions and the *a*-axis of the crystal was in the scattering plane. The incident photon energy was tuned to the absorption maximum of the Cu L_3 absorption edge at 931 eV and the polarization was circular.

Measurements were performed with two different converter designs. For both converter designs, different beamline analyser settings were chosen as a compromise between the achievable resolution and signal level. The first configuration used a 200 nm polyimide support and a 10 nm gold film as converting material grown on a 3 nm titanium buffer layer. We used the Au 4*f* lines for conversion and employed the following resolution settings: the beamline exit slit was set to 50 μ m, yielding a theoretical resolution of approximately 250 meV at the Cu *L*-edge, and the analyser slit was set to 300 μ m, giving a theoretical electron energy resolution of 150 meV. For the second converter design, we used silver 3*d* lines for the conversion, which are naturally sharper compared to the gold 4*f* lines and could thus enable a more reliable deconvolution to high resolutions. On a 200 nm aluminium substrate, a 30 nm Ag converter layer was grown on top of a 20 nm organic buffer layer. The beamline exit slit was set to 20 μ m (about 130 meV theoretical resolution) and the analyser entrance slit to 100 μ m, giving 50 meV theoretical electron energy resolution. To efficiently acquire a sufficiently large energy window over extended times, we set the analyser pass energy to 200 eV and fixed the central analysed electron kinetic energy.

Panels (a) and (c) in figure 2 show the measured PAX spectra using the Au 4f and Ag 3d levels. The results obtained with the gold converter are shown in the figures 2(a) and (b), and those obtained with the silver converter are shown in the figures 2(c) and (d).

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Figure 2. PAX data and deconvolution results. Results for measurements using a gold converter (panels (a) and (b)) and a silver converter (panels (c) and (d)). Moreover, panels (a) and (c) depict the measured PAX spectrum (black dots), converter photoemission used as deconvolution kernel (blue) and reconvolution (red) of this kernel with the spectrum resulting from the deconvolved RIXS spectra (black lines in panels (b) and (d)). Panels (b) and (d) furthermore show deconvolved Ba2342 RIXS spectra (black) compared to data taken at the ADRESS beamline [39] (orange). The inset in panel (d) depicts first to two Gaussians representing the elastic line (purple) and the magnon peak (green). The RIXS spectra are momentum-integrated within the momentum ranges that are shown in figure 3, i.e. the data from this work (black) is integrated from 0.22π to 0.46π and the data from [39] (orange) is integrated from 0.18π to 0.53π (see also supplementary information).

To obtain the pure converter photoemission spectrum, which determines the kernel for the deconvolution of the PAX spectrum, our test setup allowed for two options: the most efficient is to place the converter directly in the beam. Besides the obstacle of necessarily attenuating the signal levels by many orders of magnitude without changing the spectral properties (due to much higher efficiencies of direct photoemission compared to PAX), this option is further challenged by an intrinsically different geometry from the PAX measurements, which affects the spectral properties by introducing systematic errors to the deconvolution. For PAX, the focus of the x-ray beam is placed on the sample, while the focus of the analyser should be on the converter. In our geometry, the two foci are 3 mm apart, posing a major challenge for the alignment of x-ray and electron optics, since our test setup was originally not designed for coinciding foci. As consequence, aberrations can affect the spectra. However, for the described direct photoemission measurement of the converter, the foci may coincide, changing the optical conditions and altering the spectral influence of the aberrations thus hampering successful deconvolution. We therefore employ a different strategy to measure the converter spectrum: Retaining the PAX geometry, we employ an elastic scatterer close to the sample, so that an unaltered converter photoemission spectrum can be measured without significant change in geometry. However, the signal level in this case is much lower than in a direct measurement.

For PAX with the Au converter, we measured the Au $4f_{5/2}$ and $4f_{7/2}$ core-level photoemission spectrum by illuminating an elastically scattering part of the sample holder next to the Ba2342 sample. For the PAX measurements, we moved the sample into the x-ray beam. In our test setup with the converter fixed to the sample holder, this thus moves both components and also slightly changes the converter position towards the electron analyser, with minor effects on the spectra. The blue line in panel (a) of figure 2 shows the fit to the converter Au 4f spectrum using two pseudo-Voigt peaks (see supplementary information). The measured PAX spectra (black dots) show two small and two large, asymmetric peaks. These doublets result from the convolution of the Ba2342 RIXS spectrum with the spin-orbit split converter spectra. The small peaks originate from elastic scattering and low-energy transfer excitations of the Ba2342 excitation spectrum, while the large peaks originate from the *dd* excitations [39]. The orange line in panel (b) is the Ba2342 RIXS spectrum as previously published [39]. The black line in panel (b) shows our RIXS spectrum as a deconvolution of the PAX spectrum. The red line in (a) is a reconstructed PAX spectrum for consistency check, obtained by again convolving the extracted RIXS spectrum with the converter spectrum. The absence of deviations within the noise level between the reconstructed PAX spectrum and the measured black dots

demonstrates that the remaining differences between the extracted RIXS spectra and the true spectra are beyond the systematic and statistical limits of the current data set.

Corresponding spectra for the silver converter are shown in panels (c) and (d) of figure 2. A different Ba2342 crystal was used for these measurements. The observed photon-electron conversion originated from the silver $3d_{3/2}$ and $3d_{5/2}$ levels. The measurement time for all spectra was several hours.

To extract RIXS spectra from the PAX measurements, we use iterative deconvolution algorithms that have been benchmarked for this purpose in [27, 29, 30]. In order to suppress the artificial amplification of high frequencies in the process (which would, e.g. exceed the energy resolution limits), the estimated RIXS spectrum is regularized by convolution with a Gaussian after each iteration (see the supplementary information for details) [30]. Due to the limited measured energy window, it was challenging to properly subtract backgrounds from secondary electron scattering, optical aberrations, as well as inhomogeneities of the analyser transfer function and the detector. Their proper treatment is important for a high-quality deconvolution. Our procedure to account for these effects is detailed in the Supplementary Information.

We emphasize, however, that we use a deconvolution algorithm that does not require any prior knowledge of the spectrum. Each intensity point in the extracted spectrum is treated as a free parameter and the deviation between the measured PAX spectrum and the extracted RIXS spectrum after convolution with the kernel is minimized. The only external inputs are the regularization strength, which limits the spectral width of the features to experimentally reasonable values and thus gains physical meaning, and the number of iterations.

4. Results and discussion

Generally, the main features of the reference spectrum (orange lines in figures 2(b) and (d)) are well reproduced by the extracted RIXS spectra. As is common in RIXS measurements, the intensity of the elastic line varies between samples and measurement positions and is found to be more intense from our sample next to the Au converter. The elastic peak in the measurement with the Ag converter is found to be asymmetric, which is connected to the magnon excitation in Ba2342 at energies up to approximately 300 meV. The extracted feature can be fitted with two Gaussian peaks shifted by 91 meV with widths of 130 meV (FWHM) for the elastic peak and 205 meV for the energy loss feature, as shown in the inset of figure 2(d). The absence of this asymmetry in the Au converter data is related to the generally lower resolution and the stronger elastic line in this data set. Due to the lower resolution and higher elastic line strength, this feature is not resolved in the Au spectra. In general, spectra after deconvolution can display unphysically sharp features, sharper than supported by the quality of the measured data.

The general shape of the *dd*-excitation signatures between 1.5 eV and 3 eV energy loss is reproduced by both estimated RIXS spectra. However, the deconvolution results in three peaks of decreasing intensity with energy loss, while four peaks were previously reported [39]. The peak at the lowest energy loss in this report is less intense, but the other peaks also decrease in intensity with energy loss as in our data.

In the region of charge transfer excitations with energy losses greater than 3 eV, we find spectral weight from PAX as well as the reference spectrum. While the reference spectrum displays a smooth broad distribution, the PAX deconvolution concentrates the spectral weight into several sharper features. However, we note that this energy loss region was not fully covered with both core levels from the converter due to the small detection window (pass energy), chosen to demonstrate high energy resolution around the elastic line, and the fixed energy setting used to increase measurement efficiency: The energy loss region of the RIXS spectrum converted by the Ag $3d_{5/2}$ peak at 558.5 eV kinetic energy (figure 2(b)) ranges approximately from -1.5 eV to 10.5 eV, while the RIXS energy loss region converted by the Ag $3d_{3/2}$ peak at 552.5 eV ranges from -7.5 eV to 4.5 eV. Therefore, the charge transfer region at energies higher than 4.5 eV is only sampled by one of the two Ag 3d peaks. This, together with the low charge transfer intensity, makes this region susceptible to generating artefacts during the deconvolution. This effect resulted from the specific settings for this experiment and can be mitigated by using larger detected energy windows (larger pass energies) or the scanning mode of the analyser, when larger energy loss regions are of interest. Furthermore, with modern time-of-flight based electron analysers, a larger energy window can be acquired highly efficiently with competitive energy resolution.

In this pioneering experiment, we aimed to achieve a high energy resolution in the extracted RIXS spectrum, beyond the total resolution of the instrument. We therefore kept the regularization strength slightly lower than suggested in previous studies [30] in order to resolve sharp features. This led to the successful observation of the magnon excitation also with this method but at the expense of spurious sharpness in the charge transfer spectral region and uncertainties in the number and intensity ratio of the main *dd* excitations. Other reasons for this difference are residual uncorrected background values and slopes, as well as the limited energy detection window in the fixed analyser setup used.

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Figure 3. Momentum-resolved PAX. (a) Incident x-rays (purple) emit a fan of scattered x-rays (blue) with different wavevectors (e.g. k_1 and k_2) impinging on different positions on the converter, thereby translating momentum transferred from the sample to scattered x-rays into spatial coordinate on the converter. (b) RIXS data from the ADRESS beamline [38] (left) and RIXS deconvolved from PAX measurements (right) for a range of in-plane momentum transfers Q_{\parallel} . The energy range of the *dd* excitations is divided into three regions I, II and III, highlighted by the green, red and orange shading, respectively. (c) The mean intensities in the coloured regions of the spectra from the reference and this work (shown in panel (b)) are normalized and compared. See supplementary information for a more detailed description of the analysis of the momentum-resolved spectra.

Nevertheless, some of the differences between our approach and the reference may not be artefacts of our procedure, but may indeed be real due to a different sample growth and treatment and a different measurement geometry as compared to the reference data. Unfortunately, the experimental constraints of our setup do not yet allow for a more rigorous conclusion, but these ambiguities can be resolved with a specifically designed instrument that addresses limitations in resolution, avoids aberrations due to different foci, acquires a larger energy range, and has a more homogeneous transfer and detection function in the electron analyser.

A major advantage of PAX over RIXS measured with a grating spectrometer is the ability to acquire a large range of scattering angles simultaneously (see figure 3). In our setup, a scattering angle range from 122° to 160° is covered, corresponding to an in-plane momentum transfer Q_{\parallel} range from 0.22π to 0.46π , or about 24% of the first Brillouin zone. To assess this capability, we compare the evolution of spectral weight within the energy loss region of *dd*-excitations between reference RIXS spectra [39] (figure 3(b), left) and our extracted spectra from PAX using a gold converter by dividing the 2D detector image equally into six parts along the non-dispersive direction (figure 3(b), right). All spectra are normalized to the integrated intensity within the energy range shown.

The energy loss region is further divided into three characteristic regions between 1.5 eV and 2.5 eV energy loss, indexed I to III. The integral intensity in each region is compared as a function of the momentum transfer Q_{\parallel} after subtracting the value at the lowest Q_{\parallel} (figure 3(c)). While the intensities in region I display a decreasing intensity with Q_{\parallel} , we observe an increasing intensity with Q_{\parallel} in region II, and intensity roughly independent of Q_{\parallel} in region III. These trends are qualitatively observed both in the reference spectra measured with a grating spectrometer in sequential mode (circles) and in our parallel measurement with PAX (diamonds). We note, however, that our PAX measurement was affected by aberrations of the analyser imaging, which can be improved in a dedicated setup.

The count rate achieved by PAX is generally in the same order of magnitude as that of traditional grating-based RIXS experiments (see comparison the detailed in [29]). Specifically, in our test setup, we needed to confine the x-ray beam with baffles and thus did not use the full flux of the beamline. A count rate of about 100 counts s⁻¹ was still achieved. The measurement time for the full momentum range in the PAX data (figure 3(b)) was approximately 7.5 h that can be separated into the six shown spectra (75 min/spectrum). This is currently longer than typical RIXS acquisition times of ~30 ± 15 min per spectrum. However, we would like to emphasize that a dedicated instrument in the future can drastically reduce the measurement time. With a momentum microscopy-type electron spectrometer, the transmission can be increased by more than one order of magnitude [42].

5. Conclusion and outlook

In summary, we experimentally demonstrate the conceptual capabilities of PAX to achieve high energy resolution for RIXS at competitive signal levels using a repurposed test setup. Furthermore, the simultaneous momentum-resolved RIXS acquisition of relevant ranges of momentum transfers presents a step beyond grating-based scattering experiments. With this data set, we provide a compelling case for investing in a

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dedicated setup that will overcome current limitations and provide an instrument with energy resolution and efficiency at least competitive with large grating spectrometers at a much smaller size and cost. Such a setup can naturally also be used for modern electron spectroscopy, such as ARPES. In a dedicated setup, electron spectrometers with energy resolution better than 5 meV at soft [23, 32] and approximately 40 meV at hard x-ray photon energies (6 keV) [43] can be exploited together with high efficiency detection of large energy windows [42]. In combination with a sample environment optimized to accommodate both the sample and the converter and a highest-resolution beamline, comparable to current world-leading RIXS beamlines reaching below 30 meV resolution at the Cu *L*-edge, this provides a viable complement at much smaller footprint. Modern grating spectrometers have virtually reached current technological limitations in energy resolution, as a result of limits in achievable optics surface quality, stability requirements of the large spectrometer arm as well as detector spatial resolution [17]. PAX does not face these limitations of the spectrometer, but can build on developments in electron spectrometers. Achieving this very high resolution requires the use of converter photoemission from very sharp spectral features, like the Fermi edge of noble metals at low temperatures. The accompanying loss in conversion efficiency can be compensated by more efficient modern electron analysers [42].

Furthermore, PAX could potentially also be developed for in-situ and in-operando studies, if the pressure cell around the sample is designed in a way that the emitted photons impinge on a foil that acts as PAX converter and separates the high-pressure sample environment from the electron analyser in UHV.

Data availability statement

The data cannot be made publicly available upon publication because they are not available in a format that is sufficiently accessible or reusable by other researchers. The data that support the findings of this study are available upon reasonable request from the authors.

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Supplementary Information for

A compact approach to higher-resolution resonant inelastic X-ray scattering detection using photoelectrons

This Supplementary Information discusses in more detail the treatment of PAX (photoelectron spectrometry for analysis of X-rays) and converter photoemission spectra (sections 1, 2 and 3) which plays a crucial role for the result of the final deconvolved RIXS (resonant inelastic X-ray scattering) spectrum, how the momentum-transfer dependent spectra were obtained (section 4), and finally how the regularization strength for the deconvolution was determined (section 5).

1. Extraction of the reference RIXS spectrum

The set of RIXS spectra of the Ba₂Cu₃O₄Cl₂ (Ba2342) sample measured at the ADRESS beamline at the Swiss Light Source [1] was obtained from the authors and a subset of the spectra was selected and averaged to serve as the reference spectrum shown in the main manuscript (e.g. orange in Fig.2). We selected spectra recorded in the range of momentum transfer from 0.18π to 0.53π , which resembles that covered by the converter in the PAX geometry as closely as possible (0.22π to 0.46π). Furthermore, as the PAX measurements were recorded with circular polarization, we averaged spectra measured at ADRESS for both linear horizontal and linear vertical polarizations.

2. PAX measurement with Au converter

The 4f photoemission spectrum of the Au converter was recorded by measuring elastic scattering of the silver epoxy glue next to the sample. The intensity, in this case, was much higher in comparison to the inelastic scattering from the sample, leading to slight saturation artefacts that affect the Au 4f photoemission spectrum, apparent as a shadow partially covering the Au $4f_{7/2}$ peak and decreasing its intensity (see Figure S1 around values of x of 600). The saturation could have been prevented e.g. by closing the beamline or analyser slits, but in consequence, this would compromise the suitability of the spectrum as a deconvolution kernel for the PAX spectrum. In order to correct for the saturattion artifacts, we reconstructed the 'true' converter spectrum by adding prior knowledge about the well-known Au 4f spectrum as follows: First, the converter spectrum was fitted with two Pseudo-Voigt profiles on a background comprised of a linear slope to account for background not intrinsic to the photoemission spectrum and a Shirley function to account for background intrinsic to the photoemission spectrum. The linear slope was subtracted from the resulting spectrum. Furthermore, the obtained fit was then compared to a reference Au 4f spectrum [2] and the amplitude of the $4f_{7/2}$ peak fit was multiplied with a factor of 1.18 to match the intensity in the reference spectrum to compensate for the intensity loss caused by the saturation effects. The resulting spectrum was used as a kernel for the deconvolution algorithm, resulting in the RIXS deconvolution shown in Fig. 2(c) of the main manuscript.



The measurement time for the converter spectrum was 50 minutes. The PAX spectrum was measured for 7.5 hours.

Figure S1: **Au converter 4***f* **photoelectron spectrum.** Upper panel: Two-dimensional detector image as recorded. The shadow, discussed in the text, is visible around *x* pixel values of 600. Lower panel: Spectrum obtained from the detector image and double pseudo-Voigt fit to the data with amplitude correction (see text).

3. PAX measurement with Ag converter

The measurement of the elastic converter photoemission shows additional features next to the Ag 3*d* peaks, likely originating from surface oxidation. However, using the Ag 3*d* spectrum together with those shoulders as input for the deconvolution does not yield an appropriately overlapping reconvolution and results in strong deviations of the estimated RIXS spectrum to the reference [1] spectrum. Thus, we determine that these additional features only appear in the converter spectrum at the measured position, but do not affect the PAX measurement. The origin of these shoulders which apparently only affect the elastic photoemission is unclear. In consequence, we use only the fit to the Ag 3*d* peaks, consisting of a sum of two Doniach-Sunjic profiles (black line in Figure S2). This resulting fit is then used as input for the deconvolution together with the PAX spectrum recorded using the Ag converter. The raw 2D detector images of the PAX spectra contained a significant background. It was fitted (by excluding the peaks of the PAX spectra) and subtracted.

The converter photoemission was measured for nearly 6 hours. The PAX spectrum was measured for 10.5 hours.



Figure S2: Ag converter 3*d* photoelectron spectrum recorded from an elastic scatterer next to the sample. Upper panel: Two-dimensional detector image as recorded. Lower panel: Spectrum (light grey points) obtained from the detector image after subtraction of a linear background. The light grey line is the sum of a fit to the data consisting of four peaks: two Doniach-Sunjic peaks (dark grey) show the Ag $3d_{3/2}$ and $3d_{5/2}$ peaks and two pseudo-Voigt peaks show two shoulders, most likely originating from AgO.

4. Creation of momentum transfer-dependent spectra

Figure S3 shows the average detector image of the PAX measurements with the gold converter. The dotted lines show the edges of the 6 slices we selected to extract six momentum-dependent spectra. To account for aberrations caused by optical distortions of the electron analyser, the lines along which the slices were taken are not perfectly parallel to the energy axis, resulting in a slightly non-rectangular shape of each slice (see Figure S3). Because the converter was not in focus of the analyser, the measured signal consists of a doubled image, such that each position on the converter appears twice on the detector. This limits the precision with which we can determine the scattering angle (see Figure S3). We sliced the detector into 6 areas, where 5 unique different scattering angle regions appear. The top and bottom regions are not affected by this doubling, the regions in between though contain signals from two adjacent regions simultaneously. The average scattering angles at the position of each detector slice are also shown in Figure S3.



Figure S3: **Slicing of detector image to obtain momentum-resolved PAX spectra.** Average detector image recorded for PAX measurements with the gold converter. The dotted lines delimit the slices from which the *Q*-resolved PAX spectra were extracted. The detector signal is composed of a doubled image since the converter (diameter of 4 mm) was not in the analyser focus: The two red dotted lines mark the lower image, and the two purple lines mark the upper one. The inset shows the two images (red and purple) as well as the region where they overlap (striped) schematically. The numbers show the average scattering angle 2θ at the position of each slice.

5. Choice of regularization

Our choice of the regularization strength follows the procedure described in reference [2]. A set of PAX spectra recorded under the same conditions is split into a training and a validation set. The training set is used to estimate a series of RIXS spectra using different regularisation strengths (RS), which are then reconvolved with the converter spectrum to obtain the PAX reconstruction. The root mean squared error (RMSE) of this reconstruction with respect to the average spectrum of the validation set allows to extract the RS curves shown in Figure S4. In the left panel, the RS curves for the *Q*-integrated PAX spectra recorded with the Au converter are shown. The right panel shows the RS curves obtained for the *Q*-resolved data with the Au converter. All RS curves show the same trend of a steady decrease with smaller RS until they remain nearly constant. The crosses mark the RS which we chose for the respective data sets. We chose an RS that is `safely' in the constant regime but not far away from the onset of the rise of the RS curve, as a smaller RS would lead to unnaturally spikey estimated RIXS spectra. Since the location of the onset of the RS rise is at higher energies for worse signal-noise-ratios, the chosen RS is larger for the Q_{II} slices at the edges of the detector where the measurement statistics were worse and smaller for slices in the center with better statistics.



Figure S4: Estimation of regularization strength for deconvolution of PAX spectra. Root mean squared error (RMSE) deviation of RIXS spectra estimated from different PAX datasets for various regularization strengths (see text). Left: Regularization strength curve for *Q*-integrated PAX spectra with Ag and Au converter. Right: Regularization strength curve for *Q*-resolved PAX spectra with Au converter. Purple and red lines show the regularization strength curve for spectra obtained from the detector signal edges (see Figure S3), other colours show curves obtained from the detector centre. The crosses mark the chosen regularization strength for each data set.

6. References

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4.3 The Future of PAX

As eluded to in the conclusion and outlook section of Paper V [5], a dedicated momentum microscope (MM)-type electron spectrometer in combination with a time of flight (ToF) detection scheme is a promising prospect for PAX. Using a momentum microscope in combination with a time of flight promises an increase in count rate in comparison to the hemispherical analyser used in Paper V for two reasons (see section 2.5.1): A high voltage, applied between sample and extractor lens⁴, allows to collect the electrons emitted from the converter into the entire half-sphere, as compared to the solid angle of $\pm 19^{\circ}$ collected by the hemispherical analyser of AS-PHERE III. This contribution increases the count rate by a factor of approximately 20. Furthermore, a slit-less operation can lead to an additional increase in transmission: In a hemispherical analyser, the illuminated spot on the sample is magnified by the electron lens system onto the entrance slit of the hemisphere. Thus, the number of electrons which is lost at the entrance slit depends on several parameters, like the X-ray focus size on the sample, the angle of incidence (which increases the spot size), the magnification of the lens system and the slit size itself. In the hypothetical case of the highest transmission through the slit, the X-ray footprint on the sample and the magnification are smaller than the entrance slit width and all electrons enter the hemisphere. In the case of a low transmission with a large X-ray footprint on the sample and a small slit size, the illumination of the slit and its aperture can be approximated as homogeneous. In this case, the fraction of electrons entering the hemisphere is given by the relation of the area of the slit to its aperture. For example, a slit of $300\,\mu\mathrm{m}$ which we used during the measurements in Paper V has an approximate transmission of 1.5%. Combining the gain from a larger collected solid angle and a slit-less operation, at minimum a factor of 20 can be gained up to a factor of 1000 in the extreme case of homogeneous slit illumination. Currently, such a ToF-PAX instrument is under construction and will be commissioned at PE-TRA III after this thesis is finalized. The ToF-PAX instrument is financed by an ErUM-Pro grant of the German Federal Ministry of Education and Research to a collaboration of University of Mainz, Karlsruhe Institute of Technology (KIT), Kiel University and DESY. In the following, the suitability of such an instrument for PAX is detailed and some design choices are discussed.

A further improvement realized in the new ToF-PAX chamber is that the converter will be hosted on a separate manipulator and cryostat for rotation, motion and temperature control that is independent of the sample, as illustrated in Figure 4.2. This allows to switch between two configurations: The converter can be retracted to enable direct illumination of the sample for ARPES measurements, as shown in Figure 4.2. In the PAX configuration, the sample can be slightly retracted so that the converter can be moved in between sample and front lens (Figure 4.2b). By moving the sample along the beam direction, the scattering angle 2θ that is collected by the converter can be chosen (see panels c and d of Figure 4.2). Furthermore, both the sample and the converter can be moved independently. The possibility to cool the converter with liquid helium is especially interesting, if the Fermi edge

⁴This voltage does not affect the electronic structure of the sample as long as there is no voltage drop at the sample and no current flows through the sample, which requires homogeneous fields.

of the converter is chosen during a PAX measurement. At low temperatures, the Fermi edge is much sharper than the life-time limited 3d or 4f peaks of gold and silver, and thus potentially enables the deconvolution to higher frequencies (i.e. narrower spectral features) [5, 281, 282], as discussed in section 4.2. The expected loss in count rate from a lower conversion efficiency of the Fermi edge (about two orders of magnitude) will be more than compensated by the increase of count rate expected from the ToF-PAX instrument with the improvements mentioned above, thus opening the possibility to record very high energy resolution RIXS spectra. Moreover, the ToF-PAX instrument is very compact, especially in comparison to world-record **RIXS** spectrometers. The latter are build up to about 15 m in size, since a larger distance between spectrometer grating and detector leads to a better separation of the individual energies on the detector. Other ways to achieve this, like increasing the line density of gratings, are already at the technological limits, as discussed in detail in section 2.7.2. The most expensive items of the spectrometer itself are the grating and the detector, which may be about the same prize as a time of flight spectrometer and detector. Additionally, for such a large RIXS spectrometer, a high-precision floor is needed for the rotation of the spectrometer arm and large rooms or sometimes even extra buildings need to be build to host these large instruments. Electron spectrometers can be much smaller with a possibility to achieve better energy resolution. The ToF-PAX instrument will measure about $1 \times 1 \times 2$ m³ and be much less expensive than state-of-the-art high-resolution RIXS spectrometers.

Paper V [5] also describes the important aspect of PAX that an extended Xray-sample momentum transfer range much larger as compared to that of a grating spectrometer can be measured simultaneously. This is possible because the converter is very close to the sample, covering a much larger scattering angle (2θ) range in comparison to a grating spectrometer. For the geometry used in the PAX setup at ASPHERE III (see Figure 4.1 and Paper V), we could record a scattering angle range of 37° simultaneously. In contrast, a grating spectrometer with typical sample-grating distance of 30 cm and a horizontal width of the grating of 3 cm covers only a 2θ -range of about 6°. The implications of this difference is depicted in Figure 4.3. Here, the colour scale shows the in-plane photon-sample momentum transfer which is the projection of the total momentum transfer onto the plane that is parallel to the sample surface. The in-plane component of the momentum transfer is especially interesting for RIXS studies of high-temperature superconductors because the copper-oxygen planes are usually oriented along the a and b directions of the crystal, which are parallel to the surface, whereas the elongated c axis is oriented along the sample normal. By considering the in-plane component, intra-layer coupling in the copper-oxygen planes with direct relevance to superconductivity can be studied. The out-of-plane component can be obtained as the projection of the total momentum transfer onto the direction of the surface normal and addresses (in the case of high- T_c superconductors with the c axis orthogonal to the sample surface and related compounds) the interlayer-coupling between the copper-oxygen planes [191]. Using a momentum microscope for PAX enables recording electron emission from two spatial dimensions on the converter. One of them is the dimension of the principal scattering plane (the plane in which the configurations of Figure 4.2 are



Figure 4.2: ARPES and PAX configurations of the new ToF-PAX instrument. In the ARPES configuration (panel a) of the ToF-PAX instrument, the sample (grey) is illuminated by the X-ray beam (purple) under grazing incidence with a working distance A from sample to spectrometer front lens (light grey) of 7.5 mm. Switching to the PAX configuration (panel b) requires moving the sample (and X-ray focus) away from the front lens and inserting the converter at the working distance A. The converter (yellow, 4 mm diameter) collects RIXS photons from a range of scattering angles 2θ (blue triangle), which translates to a range of simultaneously probed in-plane momentum transfers $\dot{k_{\parallel}}$ (see main text and Figure 4.3). The accessible momentum transfer range can be increased by additionally rotating the sample angle θ (grey). Panels c and d show a similar situation, but with the sample moved to different positions along the X-ray beam. This changes the scattering angle range which is collected by the converter and thus the probed in-plane momentum transfer, as shown in Figure 4.3. At large 2θ values (panel d), the maximum accessible sample angle θ_{\max} is restricted to an in-plane momentum transfer of approximately $\left|\vec{k_{\parallel}}\right| = 0$.



Figure 4.3: In-plane momentum transfer as a function of sample angle θ and scattering angle 2θ for an incident photon energy of 930 eV, corresponding to the copper L_3 edge. The momentum transfer range marked by the black-dashed rectangles b, c and d was inferred from the ToF-PAX sample geometries shown in the respective panels of Figure 4.2. Other regions of the θ -2 θ space can be accessed by choosing positions not explicitly shown here (black-dotted triangle). Without rotating the sample, a given ToF-PAX geometry in Figure 4.2 simultaneously covers an in-plane momentum transfer range that extends from the left to the right edge of the respective rectangle (grey lines). The vertical position can be chosen with the sample angle rotation θ , with the extremes given by the upper and lower edge of a rectangle. The green-dotted triangle marks the approximate range that is in principle accessible by scanning θ and/or 2θ a typical RIXS spectrometer. However, only a relatively narrow momentum transfer range is probed simultaneously (light green line; see also main text). The turquoise line marks the momentum range probed simultaneously by the PAX setup in the ASPHERE III chamber as described in Paper V [5]. The bars next to the colour scale show the in-plane momentum transfer range which is covered by the shapes of respective colour and line style.

drawn), but also in the other dimension, information on momentum transfer which is directed out of this plane can be accessed.

Figure 4.3 shows the in-plane momentum transfer as a function of sample angle θ and scattering angle 2θ . The dashed, turquoise line marks the range that was measured simultaneously in the setup at ASPHERE III described in Paper V (see also Figure 4.1), which was enough to cover about a quarter of the first Brillouin zone of the Ba2342 sample. The black-dashed rectangles show the approximate in-plane momentum transfer accessible with the ToF-PAX instrument for the sample positions shown in Figure 4.2. The horizontal 2θ dimension of such a rectangle

can be measured simultaneously for one sample position (grey lines), whereas the vertical position along the rectangle is determined by the sample angle θ . From Figure 4.3 one can see that a fairly large momentum transfer range can be accessed, and that, in principle, the three sample positions shown here can cover a large part of the accessible momentum transfer range. By moving the sample to other positions, not shown in Figure 4.3, approximately the range of the black-dotted triangle can be accessed. The green triangle in Figure 4.3 shows approximately the momentum transfer range that can be accessed in general with a grating-based **RIXS** spectrometer. However, not all instruments are able to access the entire range. As discussed in section 2.7.2, the gratings of RIXS spectrometers usually only cover a small fraction of the solid angle because they are typically several tens of centimetres away from the sample. For the momentum transferred from photon to sample, this means that only a very narrow range of about 6° is probed for a given measurement geometry, as shown by the light green line for the example of $\theta = 100^{\circ}$ and $2\theta = 132^{\circ}...138^{\circ}$. To access a larger momentum transfer range, grating spectrometers use a sequential acquisition strategy: A certain geometry is chosen by setting the sample scattering angles, a RIXS spectrum is acquired and then the next geometry is chosen by either rotating the sample or scattering angle, before acquiring the next spectrum. With PAX, this procedure can be parallelized because of the short distance from the sample to the analyser (here the converter).

In summary, the new ToF-PAX instrument allows to access a large part of the $\theta - 2\theta$ space. A significant part of the $\theta - 2\theta$ space can be probed simultaneously, while the rest is accessible through additional rotation of the sample and movement of the sample along the incident X-ray beam. A high energy resolution will be enabled through a higher count rate which in turn enables the use of spectrally narrow features - like the Fermi edge at cryogenic temperatures - for conversion. Lastly, with the inclusion of separate manipulators for the sample and the converter, the new chamber is designed to be able to quickly switch between measurement geometries for PAX-RIXS (with the converter inserted) and ARPES (with the converter retracted), as shown in panels a and b of Figure 4.2. RIXS and ARPES probe different aspects of the electronic structure: The former is especially well-suited to study collective low-energy excitations and coupling constants of different degrees of freedom, like the electron-phonon coupling (see section 2.7), whereas the latter probes the single-particle spectral function and is a well-established technique to map the band structure or Fermi surface [74]. With the new PAX instrument, both methods can be combined for measurements performed on the physically same sample and sample spot. Switching between the configurations only requires short motor movements without the need to break vacuum. This will enable the study of inhomogeneities and separated phases in quantum materials with two complementary probes.

5 Conclusion

In this thesis, new soft X-ray methods for the study of the complexity of quantum materials are presented. Multidimensional and multimodal experimental capabilities allow to adapt the measurement approach to the research question posed by a specific quantum material, while soft X-rays selectively address core resonances or probe the crystal structure. Such studies of quantum materials in several dimensions require efficient use of the photons provided by synchrotron radiation and free-electron laser sources. Without parallelized measurement schemes, experiments become unfeasible within the limited time at large-scale instruments - despite the provided high spectral brightness. In the experimental schemes that were demonstrated in this work, the measurement efficiency is realized by parallelizing the acquisition in multiple dimensions. Studied phenomena in quantum materials entail an investigation of the thermally driven IMT of vanadium dioxide (VO₂), phase separation in $Y_{1-x}Ca_xTiO_3$ as well as the laser-induced IMT in magnetite (Fe₃O₄). In the following, I will first conclude on the results achieved with the RIXS imaging method and techniques derived from it and then on the PAX method.

RIXS imaging aims to fulfil Goal 1 (Add spatial resolution to RIXS) that was stated in the Introduction (chapter 1) by using an off-axis transmission zone plate to combine sample imaging with several different X-ray probes. The inclusion of multiple soft X-ray techniques, like XAS, XES, RIXS, RXD and (time-resolved) XRD extends Goal 1 by adding the achieved spatial resolution of 2 µm also to other probes of electronic and geometric structure and by adding temporal information. Furthermore, this setup can efficiently use the entire photon energy bandwidth provided by the beamline monochromator by keeping the beamline exit slit open and by parallelising the acquisition of the resulting range of incident energies. Future improvements of the throughput and spatial resolution are discussed in the Outlook (chapter 6).

The potential of the RIXS imaging technique was confirmed by tracking the thermally induced IMT in VO_2 microsquares with PFY-XAS. This study found that the phase transition temperature is reduced by 1.2 K at the edges of the microsquares. An important implication for the use of quantum materials in microelectronic devices is that pre-characterisation techniques with the ability to study how properties of quantum materials change upon structuring on the microscale are required.

Transferring the RIXS imaging technique to soft X-ray diffraction enabled the study of separated phases in $Y_{1-x}Ca_xTiO_3$ (with x = 0.37). With this full-field diffraction imaging approach, domains of insulating and metallic phases with distinct crystallographic structures were observed to coexist in curved, pinned stripes with a period of approximately 13 µm and lengths exceeding 1 mm. The origin for the formation of these stripes was found to be a periodic variation in the Ca and Y concentrations, likely arising during the crystal growth procedure. By further

studying this effect in the future, control of the (potentially anisotropic) macroscopic conductivity properties of this system may be in reach.

A further derivate of the RIXS imaging setup was used at the free-electron laser in Hamburg (FLASH) in a time-resolved IR pump-RXD probe study of the laserinduced IMT in magnetite. This setup for time-to-space mapping can be used to simultaneously acquire a pump-probe delay range of several picoseconds and a pump laser fluence range of up to one order of magnitude. In an optimized setup, single-shot acquisition of a full delay-fluence data set could be used to circumvent measurement uncertainties arising from SASE, sample damage, jitter or samples with non-reproducible ground states.

The above examples show that the use of zone plates for X-ray spectroscopy, scattering and diffraction studies does not only add spatial resolution to RIXS, but also to a suite of other techniques.

The second experimental approach which was further developed is the revitalized technique PAX. In this thesis, the potential for PAX to measure high-resolution RIXS was discussed. The general structure of the PAX-RIXS spectrum of the cuprate Ba2342 matched the RIXS reference and a magnon excitation was observed as a shoulder to the elastic line peak. PAX enables the simultaneous measurement of a range of sample-photon momentum transfer corresponding to approximately a quarter of the first Brillouin zone (for the Ba2342 cuprate sample). As PAX is performed in electron spectrometers, a PAX instrument is small and less expensive in comparison to large, high-energy-resolution RIXS spectrometers and can even be used as a flexible, semi-permanent endstation, i.e. it is much easier to integrate into the environment of a large-scale research facility. In summary, the method of PAX aims to fulfil Goal 3 (Achieve an energy resolution of $\Delta E = 1 \text{ meV}$) formulated in the Introduction (chapter 1). A new experimental endstation developed specifically for PAX has the potential to continue improving the currently achieved energy resolution. Moreover, this instrument will allow to quickly switch between PAX and ARPES measurement modes without breaking vacuum, enabling multimodal studies of quantum materials with fundamentally different probes on the same sample spot at similar conditions, which is the fulfilment of Goal 2 (Combine RIXS with ARPES).

6 Outlook

This thesis has presented two experimental approaches - PAX as well as zone platebased imaging combined with spectroscopy, scattering or diffraction - that align with the direction which contemporary quantum materials research is turning to: Investigating quantum materials on nanometre length scales, millielectronvolt energy scales and femtosecond time scales with a combination of different techniques that are part of the experimenter's toolbox. While the suitability of approaches for the study of quantum materials has been presented in first experiments, their development has only just begun.



Figure 6.1: Publications (blue) and citations (red) related to RIXS. Results were obtained by searching the database 'scopus' (https://www.scopus.com/) using the appearance of the terms 'resonant inelastic x-ray scattering' and 'rixs' in the fields keywords, title and abstract. Data from [35].

In the Introduction (chapter 1), the increasing number of publications and citations concerning 'quantum materials' in recent years was shown, see Figure 1.1. In contrast, the publication output and citations numbers in the field of 'RIXS' is plateauing in the last few years (see Figure 6.1). While the reasons for this may be complex and difficult to pinpoint, a partial contribution might come from the fact that the RIXS instrument development and improvements in energy resolution are slowing down, as described in sections 2.7.2 and 2.8. In consequence, also the supply of ever more collective excitations and new materials that become accessible with these improvements is slowly fading. With the development of RIXS imaging to add spatial resolution to soft X-ray methods and PAX aiming at high-energy resolution RIXS, this thesis describes fundamentally different approaches to improvements of **RIXS**, bringing the promise of new insights into the complexity of quantum materials.

One step which can be taken in the near future concerns the observation of metallic and insulating stripe domains in $Y_{1-x}Ca_xTiO_3$ (x = 0.37). To our knowledge, this observation is the first proof of spatial variation of chemical inhomogeneity [3]. Therefore, several questions arise which can be answered in future experiments without major alterations to the experimental setup: How are the stripes shaped along other crystal directions? How ubiquitous is the observed effect in mixed-valence perovskite systems? Are stripes also present if the Ca-doping x is changed? How about related systems where Y is replaced with other trivalent elements, like different rare-earth elements [261]? If our conclusion is true that the stripes originate from convection dynamics in the crystal growth process, there are several immediate questions: How do fabrication parameters influence the stripe pattern? Furthermore, it is reasonable to assume that the stripes are the origin of anisotropic resistivity behaviour which has been found in $Y_{1-x}Ca_xTiO_3$ [299]. If this is the case, can we learn to shape and structure this material to design its properties?

A future methodological improvement to the RIXS imaging setup concerns the spatial resolution which is currently limited by the sample magnification factor. Zone plates are able to achieve a resolution much better than 2 µm. The magnification can be increased by a factor of up to ten with a zone plate design that allows to bring the optic closer to the sample and potentially a larger zone plate-detector distance. Thus, a resolution around 200 nm could be achieved. There are several examples for quantum materials with domain sizes around or just below 1 µm, which can currently not be resolved but become accessible with this envisioned improvement. Examples are high-temperature superconductors which show regions with increased charge-density wave order and regions with an increased concentration of oxygen atoms located at interstitial lattice sites [54, 112, 113, 300]. Also in VO₂, metallic and insulating domains could be resolved with the improved spatial resolution [226]. Based on the results obtained in Paper II [2], this would enable an investigation of how the phase transition properties of the individual phases in VO_2 change as a function of structure size and shape. In $Y_{1-x}Ca_xTiO_3$ and related systems, inhomogeneities within the metallic and insulating stripes, which can currently not be resolved, could be investigated in more detail. One caveat of a larger magnification factor is the reduction of the field of view (which scales quadratically with the magnification if the entire detector is illuminated). Potentially, also the energy and spatial resolution degrade quicker for photon energies that are not perfectly in focus of the zone plate (see Paper I [1] and its supplementary information). More detailed dependencies result from the design parameters of the higher-magnification zone plate.

With the upgrade to PETRA IV, an increase in spectral brightness by a factor of approximately 10 is envisioned for the soft X-ray range (see Figure 2.4 and [118]). Additionally, if the focusing capabilities of the soft X-ray beamline at PETRA IV allow to bring the spot size on the sample to a few hundred nanometres, the linear illumination zone plate, used in the RIXS imaging setup [1] to focus the incident beam below 1 µm in the horizontal dimension, could be omitted. This would increase the throughput of the method by another factor of 10, allowing to study the behaviour

of individual phases in an increased number of dimensions within a reasonable measurement time. For example, with the RIXS imaging method, RIXS maps could be recorded for every illuminated spot along the line focus. This requires scanning of the incident photon energy and zone plate position along the optical axis. Lastly, to map a larger region of the sample, a scan of the sample position in direction perpendicular to the line focus is required. With the parallelized acquisition of the setup and the increased photon flux, measuring such a dataset in a reasonable amount of time should be feasible at PETRA IV.

Concerning the PAX technique, the next steps are to explore the achievable energy resolution with the expected improvements in signal levels of the new ToF-PAX endstation and by using the Fermi edge of e.g. platinum for conversion as well as the demonstration of the combination with ARPES. The improvements in photon flux provided by PETRA IV will further facilitate to advance towards the ambitious Goal 3 of an energy resolution of 1 meV. The combination of a high energy resolution in resonant inelastic X-ray scattering (RIXS), the potential for complementation with ARPES and the compactness and cost reduction of the ToF-PAX chamber bear the potential to open up PAX-RIXS (with ARPES) to a broader scientific community.

When the PAX technique and the deconvolution procedure have become established, a next step could be to combine it with the RIXS imaging technique: A zone plate could image an extended illumination spot from the sample onto the converter. PAX electrons emitted from different spots on the converter would then be imaged onto the detector and encode RIXS spectra from the different sample spots. Thus, this would constitute a way of measuring full-field imaging **RIXS** information. A ToF-type PAX instrument is ideally suited because the sample can be imaged in the two lateral dimensions and the time of flight of the electrons encodes the PAX spectrum from each spot. Such an approach would imply that the PAX spectra from many small regions on the detector image (even down to the individual pixel level) need to be deconvolved separately. The most critical aspect of this idea is the count rate, which would be much smaller in comparison to a current PAX experiment, because the zone plate has an efficiency of 10% to 15%. Furthermore, the collected solid angle of **RIXS** photons would be smaller, since the zone plate needs to be further away from the sample (at least a few centimetres) in comparison to the short sample-converter distance of a few millimetres in the current PAX configuration. Lastly, acquisition times would increase because enough statistics need to be collected for every PAX spectrum in every region on the detector image to warrant a good deconvolution. If these challenges can be overcome, the implementation of a zone plate would replace the momentum transfer information (which in PAX is obtained by imaging the converter onto the detector) with spatial information. Depending on the sample, either spatially-resolved information or momentum-resolved information could be investigated. Switching between the two modes would be done by inserting or removing the zone plate. The spatial information would be preferred to study coexisting domains and their formation, e.g. close to the insulator-to-metal transition temperature, whereas momentum information could be recorded from homogeneous samples, e.g. the pure phases far away from the insulator-to-metal transition temperature.

In the coming years, the analytical tools offered by the methods presented in this thesis can be optimized and applied to a more diverse range of quantum materials. The increased brightness of fourth generation synchrotron sources, with PETRA IV at the forefront, will allow us to continue increasing the complexity and versatility of our tools in order to adapt to the research questions posed by quantum materials.

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Acronyms

- Fe_3O_4 magnetite. iv, vi, 2, 7, 11, 12, 27, 30, 36, 78, 79, 121, 122
- **VO₂** vanadium dioxide. iii, v, 3, 6, 7, 9, 11, 36, 55, 56, 121, 124
- **2D-RIXS** two-dimensional RIXS. 41
- AFM antiferromagnetic. 96
- ARPES angle-resolved photoemission spectroscopy. iii–vi, 5, 7, 17, 21, 23–25, 34, 97, 98, 115, 117, 119, 122, 125
- **Ba2342** Ba₂Cu₃O₄Cl₂. 97, 118, 122
- CCD charge-coupled device. 32, 35
- CDW charge-density wave. 12, 124
- CMOS complementary metal-oxide-semiconductor. 32
- CO charge order. 16, 96, 97
- COO charge and orbital order. 79
- **DoS** density of states. 5, 19
- EDX energy-dispersive X-ray spectroscopy. 65
- **EELS** electron energy loss spectroscopy. 6, 30, 31
- ESCA electron spectroscopy for chemical analysis. 23
- **EY** electron yield. 20, 21, 35
- FEL free-electron laser. iv, vi, 13–16, 35, 36, 77, 78, 95, 121
- FELs free-electron lasers. iii, v, 4, 7, 13–15, 31, 79, 80, 95
- FLASH free-electron laser in Hamburg. viii, ix, 13–15, 36, 122
- FWHM full width at half maximum. 13, 15, 99
- **FY** fluorescence yield. 20, 21, 23, 32, 35, 98
- GMD gas-monitor detector. 77

- HSQ hydrogen silsesquioxane. 39
- HTO high-temperature orthorhombic. 65
- **IMFP** inelastic mean free path. 21, 23, 24, 98
- **IMT** insulator-to-metal transition. iii, 2, 3, 7, 9, 11, 12, 27, 35, 36, 55, 56, 78, 79, 121, 122, 125
- IMTs insulator-to-metal transitions. iii, iv, 2, 3, 9, 16
- **INS** inelastic neutron scattering. 5, 31
- **IP** ionization potential. 18
- **IR** infrared. iv, 3, 6, 7, 15, 31, 79, 80, 122
- **IRIXS** intermediate X-ray energy RIXS. 32
- **IXS** inelastic X-ray scattering. 30
- **IXS2019** 11th international conference on inelastic X-ray scattering. 7
- KB Kirkpatrick-Baez. 98
- **KEPCO** Korea Electric Power Corporation. 3
- LCLS Linac Coherent Light Source. 95
- LTM low-temperature monoclinic. 65
- LTO low-temperature orthorhombic. 65
- MCP multi-channel plate. 25
- **MM** momentum microscope. 25, 95, 115, 116
- MUSIX multidimensional spectroscopy and inelastic X-ray scattering. 35
- **PAX** photoelectron spectrometry for the analysis of X-rays. iv, vi, 7, 21, 34, 95, 97–100, 115–119, 121–123, 125
- **PES** photoelectron spectroscopy. 21, 23, 24
- **PETRA III** Positron-Elektron-Tandem-Ring-Anlage III. vii, viii, 13, 14, 25, 32, 36, 65, 97, 115
- PETRA IV Positron-Elektron-Tandem-Ring-Anlage IV. 13, 14, 124–126
- **PFY** partial fluorescence yield. 20, 55, 121
- **RIXS** resonant inelastic X-ray scattering. iii–vi, 5–7, 15, 17, 18, 21, 23, 27–36, 39, 41, 42, 55, 56, 65, 95–97, 99, 100, 116–119, 121–125, 155, 156

- **RXD** resonant X-ray diffraction. 5–7, 12, 15, 17, 18, 26–29, 35, 36, 39, 79, 121, 122
- **SASE** self-amplified spontaneous emission. 14, 15, 77, 122
- STEM scanning transmission electron microscopy. 31
- STXM scanning transmission X-ray microscopy. 6, 31
- TFY total fluorescence yield. 20
- **ToF** time of flight. 25, 96, 115–119, 125
- UHV ultra-high vacuum. iv, 5, 24, 34
- **UPS** ultraviolet photoelectron spectroscopy. 21
- UV ultraviolet. 6, 21, 23, 31
- **XAS** X-ray absorption spectroscopy. iii, v, 5–7, 11, 15, 17–19, 23, 27, 29, 31, 32, 34–36, 39, 55, 121
- **XES** X-ray emission spectroscopy. iii, 6, 7, 17, 18, 27, 35, 36, 121
- XMCD X-ray magnetic circular dichroism. 35
- **XPS** X-ray photoelectron spectroscopy. 5, 15, 17, 18, 21, 23, 24
- XRD X-ray diffraction. iii, vi, 6, 12, 35, 65, 121

Eidesstattliche Versicherung

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