X-ray imaging and spectroscopy by single-pixel detection

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<u>Abstract</u>

X-ray measurements have a wide range of applications in fields such as basic science, hightech industries, medicine, and security. The ability of x-rays to penetrate deep into objects enables internal detection, and their high energy and short wavelength facilitate atomic-level analysis of internal samples. However, x-ray measurement poses challenges. The production of optical components like lenses and mirrors in the x-ray range is complex due to the very low refractive index in this range.

During my PhD research, I developed novel imaging and spectroscopy methods that enhance the performance of standard techniques. I utilized ghost metrology, which employs single pixel detection and correlation. Through various experiments, I demonstrated its usefulness in diverse aspects within the x-ray regime.

Firstly, in the field of imaging, I pioneered x-ray ghost imaging without the need for a camera. This experiment showcased the advantage of ghost imaging in terms of spatial resolution, which could be determined solely by the features of a mask. By implementing this technique, I opened up the possibility of achieving high-resolution x-ray imaging through a simple and practical system, as detailed in my first paper.

In my second experiment, I developed a ghost fluorescent method. Instead of measuring transmission, I reconstructed chemical element maps by measuring the fluorescent emission. Compared to the standard XRF technique performed through raster scanning, my method offers the advantage of improved resolution and significantly reduced scan requirements using compressed sensing algorithms. In my second paper, I demonstrated that even with a tenth of the number of pixels, chemical mapping could be accurately reconstructed. This capability enables fast and efficient chemical mapping.

My third paper emphasizes the strength of ghost metrology in the presence of inherent system noise. X-ray free electron lasers (XFEL) spectroscopy is a leading and highly relevant field that enables the observation of ultra-fast dynamics at the atomic level. However, pulse-to-pulse spectral variations challenge accurate spectrum measurement. In my experiment, I demonstrated the potential of utilizing these variations for ghost modality in the spectral domain. I showed that by employing ghost spectroscopy, it is possible to overcome the tradeoff between duration and resolution. This technique, which combines a straightforward system with exceptional capabilities, allows for the measurement of effects that are at the forefront of research.

In conclusion, the utilization of ghost metrology offers numerous advantages in the x-ray regime, particularly in the fields of imaging, fluorescence, and spectroscopy. Although further development is necessary, these capabilities possess the potential to become powerful tools for measuring currently unquantifiable effects.

Chapter 1: Background

1.1 X-ray strengths

On November 8, 1895, Wilhelm Conrad Röntgen made the groundbreaking discovery of x-ray radiation in his laboratory at the University of Wurzburg. Just six weeks later, he published his famous paper [1], featuring the iconic image of his wife's hand shown in Figure 1(A). The remarkable ability of x-rays to penetrate the human body quickly led to their development as a powerful tool for medical and security imaging, which continues to serve the industry and hospitals to this day. It took nearly a decade to establish that x-ray radiation is part of the electromagnetic wave spectrum [2], and due to their high frequency, x-rays can penetrate materials containing light atoms to significant depths.



Figure 1: (a) First demonstrations of x-ray imaging, (b) diffraction, and (c) the renowned Moseley table illustrating the dependence of fluorescence radiation on the atomic number.

While Röntgen initially explored the penetration capabilities of x-rays, he likely had no idea how extensively they would revolutionize the world. Around twenty years after his seminal paper, in 1912, Max von Laue demonstrated the ability to measure diffraction from atomic structures [3]. This phenomenon was later explained by the father-son duo Bragg, attributed to the extremely short wavelength of x-rays [4]. This marked the birth of crystallography, which would eventually lead to the revelation of DNA's helical structure in the 1950s [5], serving as the cornerstone of all biological research. The first x-ray diffraction pattern is depicted in Fig. 1(B).

The strong correlation between diffraction angle and wavelength allowed Bragg and Bragg to develop the x-ray spectrometer, which enabled Henry Moseley to discover that the emitted x-ray radiation from each chemical element is a unique energy proportional to its atomic number [6]. This ability facilitated easy detection and exploration of the elemental composition of materials, finding applications in a wide range of research and industrial fields. The renowned Moseley table is presented in Figure 1(C).

However, the unique emission spectrum not only serves as a means to identify chemical elements but also provided details about the electronic structure of the atom. Thus, it was the first experimental evidence for Niels Bohr's theory [7], as demonstrated by Moseley's work [6] and later by Manne Siegbahn [8]. This marked the birth of x-ray spectroscopy.

The power of x-ray radiation is underscored by the fact that all the individuals mentioned above—Röntgen, the Braggs, Laue, Siegbahn, as well as Watson, Crick, and Bohr—were awarded Nobel Prizes for their inventions (although, unfortunately, Moseley died in World War I, otherwise he likely would have been awarded as well). The remarkable capabilities of x-rays were revealed over a century ago, but significant progress has since been made with the development of powerful x-ray sources, taking the capabilities of x-rays to new heights.

1.2 X-ray sources

Röntgen initially used a simple anode in his experiments. The process involved applying a high voltage to generate a beam of electrons that would strike the heavy-element anode. The core electrons would be ejected, and electrons from higher energy levels would transition to the core level, resulting in the emission of x-ray radiation. This method proved effective for basic imaging and spectroscopy systems but had its limitations. The anode would heat up rapidly, leading to a short lifespan and limited flux. Furthermore, the energy distribution was restricted to a single emission line.

Although several improvements have been made to anode capabilities over the years, a significant advancement came with the invention of synchrotron radiation in the late 1960s. In a synchrotron beamline, electrons are guided along a circular trajectory by a constant magnetic field, generating x-ray radiation. While an anode can achieve a brilliance of 10^{15} [c.p.s / (mrad²mm²0.1% BW)] the brilliance of fourth-generation synchrotrons can be ten orders of magnitude higher. Additionally, synchrotrons offer a broad range of energies that can be controlled by the machine's properties. The powerful capabilities of synchrotrons opened up new avenues of exploration in previously uncharted territories. A notable example is Ada Yonath's Nobel Prize-winning research on Ribosome mapping in 2009 [9]. Another field that

emerged due to synchrotron radiation is the analysis of fine structures in x-ray absorption and emission spectra, which provides valuable information about atomic interactions with the molecule.



While synchrotrons have been instrumental for many researchers, they still have limitations in terms of coherence and flux. A significant development occurred a decade ago with the first X-ray free-electron laser (XFEL) [11]. In XFELs, a relatively long indulator serves instead of a cavity, and the interaction between a bunching electron beam propagating at relativistic velocity and the radiation emitted from electron fluctuations leads to radiation amplification, resulting in a powerful and short pulse. XFEL radiation offers a brilliance of approximately 10^{35} [c.p.s/(mrad²mm²0.1% BW)], pulse durations close to the attosecond range, and higher transverse coherence compared to other sources. As a result, XFELs are crucial for investigating ultrafast dynamic processes at the molecular and atomic levels and have the ability to perform x-ray diffraction on sensitive samples without adversely affecting them.

1.3 X-ray challenges

While the abilities of x-rays are remarkable, there are inherent challenges when dealing with high-energy photons. As discussed earlier, x-ray photons interact with atoms due to their energy being on the same scale as ionization energy. While this interaction is useful, it can also

be hazardous as it damages atoms and poses risks to the human body or other sensitive biological samples.

However, the main limitation arises from the extremely low refractive index in the x-ray regime. The difference in refractive index between x-rays in a material and in a vacuum is approximately 10⁻⁶, making it exceptionally challenging to manipulate and control x-rays. Traditional refraction lenses are non-existent, Mirror cavities are not optimal, and light modulators remain a distant aspiration.

Consequently, optical devices in the x-ray regime differ significantly from those in the optical regime. Even more than a hundred years after Röntgen's experiment, fundamental limitations persist in x-ray applications, even with the use of powerful sources. Therefore, methods proposing simpler setups hold immense promise. In the following two chapters, I will describe some of these limitations and discuss how my approach addresses them.

Chapter 2: Introduction

In the previous chapter, I provided a general overview of the strengths and challenges of x-ray detection, as well as various x-ray sources. In this chapter, I will introduce the method of ghost metrology (GM) that I employed to address these challenges. Firstly, I will provide a general explanation of GM. Subsequently, I will delve into three distinct x-ray applications, highlighting their limitations and how GM can offer valuable assistance. While I will provide a general understanding of why GM is beneficial here, a more detailed description of the experiments I conducted and the benefits I demonstrated will be presented in the following chapter.

2.1 Ghost metrology

GM, correlation measurement, structure illumination, compressive sensing, and single-pixel detection are different terms used to describe the same fundamental idea. Initially, GM was explored as a quantum entanglement effect [12], but it was later discovered that it can be achieved classically [13], offering numerous advantages [14] even when using thermal source. A typical setup for spatial domain ghost imaging (GI) is illustrated in Figure 3. A structured beam is split into two identical beams: one passes through the sample and is detected by a single-pixel detector, while the other is measured by a multi-pixel detector. By repeating this process for various structures, the sample can be reconstructed using a correlation protocol.



Figure 3: Experimental setup for traditional ghost imaging. A homogeneous beam passes through a mask to create a unique structure. The beam is then split into two arms: one where the multi-pixel detector measures the spatial distribution after propagation, and the other where the beam interacts with the object and is detected by a single-pixel detector. Through a correlation protocol, the transmission image of the object can be reconstructed.

Ghost imaging has primarily been investigated in the optical regime [15], and researchers have demonstrated its applicability in various domains such as 3D [16], temporal [17], spectral [18–21], and polarization [22]. Furthermore, it has been implemented using different types of radiation, including radio waves [23], infrared [24], terahertz [25], electrons [26], and atoms [27]. The first experiment reporting GM in the x-ray regime was conducted in 2016 [28], opening up a promising area of research [14]. In my work, I experimentally demonstrated the utility and effectiveness of GM in this range, leveraging its unique advantages to address specific limitations, as elaborated upon below.

2.2 X-rays applications

At first glance, performing measurements with a single-pixel detector may seem cumbersome. It would be more straightforward and faster to directly measure the data using a multi-pixel detector located behind the object. However, it has been discovered that there are specific scenarios where GM offers significant advantages. In the following sections, I will present the experiments I conducted to demonstrate the potential of GM in x-ray imaging, fluorescence, and spectroscopy. I will provide the motivation behind utilizing GM in each of these techniques.

2.2.1 X-ray imaging with tabletop source

X-ray transmission imaging relies on a simple setup where an x-ray beam passes through the object, and a camera detects the photons per pixel. In regions of the spatial position where an absorbing sample is present, fewer photons are detected. X-rays offer advantages such as relatively long penetration depth compared to electrons and the potential for high resolution due to their short wavelength, which could theoretically reach angstrom scale.

However, a fundamental challenge in x-ray imaging is the absence of high-quality lenses. While techniques have been successful in imaging nanoscale objects using high coherence sources like synchrotrons or free-electron lasers [29,30], these methods are not practical for medical or security applications. Without lenses, the image resolution is limited by the pixel size, which is determined by production capabilities.

Through the utilization of GM, I have demonstrated that the resolution can be solely determined by the features of the mask. This approach is implemented using computational ghost imaging (CGI), where the illuminated structure is known [13,31], eliminating the need for a multi-pixel detector. In my research, I proposed and validated the effectiveness of using a fabricated mask to generate the illuminated structure, resulting in spatial resolution dependent solely on the feature size of the mask. While industry-standard x-ray machines typically achieve resolutions of 200 microns, I achieved resolution of around few microns.

2.2.2 X-ray fluorescence imaging

Since Moseley's groundbreaking work, x-ray fluorescence (XRF) has emerged as a powerful technique for identifying and mapping the chemical compositions of samples. The process is as follows: X-ray radiation is used to excite bound electrons in a sample. When the electrons return to their ground state, x-ray radiation at lower photon energies that correspond to the characteristic atomic lines is emitted. The spectrum of this emitted radiation, known as the fluorescence spectrum, can then be used to identify and characterize the composition of the sample.

Since the fluorescence radiation is omnidirectional, two-dimensional chemical mapping is challenging and cannot be performed directly by a camera. Typically, the beam is focused in conventional XRF, and a raster scanning approach is employed to scan the sample point by point. However, it is time-consuming and limited by focusing capabilities at high photon energies. In my research, I proposed an alternative method inspired by GI. By measuring the fluorescence signal using an energy-resolved detector instead of the transmission signal, I reconstructed a two-dimensional chemical map, and two key advantages were demonstrated. Firstly, the resolution is determined by the mask's feature size, unlike spot size limitations in standard XRF. Second, by employing compressed sensing [32] or artificial intelligence [33], the number of repetitions can be significantly reduced, shortening the measurement time compared to raster scanning. This approach maintains the flexibility of standard XRF, allowing the detector to be positioned anywhere around the sample, including in reflection, and enabling the use of a one-sided apparatus.

2.2.3 X-ray spectroscopy at XFEL

Short-wavelength spectroscopy plays a crucial role in determining the electronic structure of materials, providing valuable element-specific insights into charge and spin structures, as well as bonding configurations. This information is essential for understanding the functionality of materials [34]. When applied in free-electron lasers (FELs), x-ray and extreme ultraviolet (XUV) spectroscopy enable the study of dynamic processes through pump-probe schemes [35]. However, FEL pulses generated via self-amplified spontaneous emission (SASE) typically exhibit broad bandwidths with random variations in pulse energy and spectra from shot to shot.

Consequently, it becomes necessary to measure the spectra both before and after the sample on a shot-to-shot basis. An alternative approach for conducting absorption spectroscopy with FEL radiation involves using narrowband radiation and measuring the total transmitted intensity after passing through the sample.

The broad bandwidth pulse strategy offers several advantages, such as the ability to measure broad spectra ranges without the need for scanning the central emission wavelength and higher flux availability. Therefore, this approach can be significantly faster than the narrow bandwidth approach. Unfortunately, simultaneously employing two single-shot spectrometers is challenging and time-consuming, as they rely on crystals or gratings and are highly sensitive to angles. Furthermore, this approach is limited to transmissivity samples.

In this context, the variability of pulse characteristics from shot to shot makes GM an attractive solution. By employing GM in the spectral domain, the radiation spectrum incident on the sample is measured and correlated on a shot-by-shot basis with the intensity detected by a post-sample detector. By utilizing multiple input pulses with varying spectral distributions, the absorption spectrum of the sample can be reconstructed.

This setup involves only one spectrometer positioned in front of the sample, along with a single-pixel detector without spectral resolution placed behind it. In my experiment, I directly compared the measurement times and spectral resolution of our approach with those obtained through scanning the central emission wavelength of the SASE and using a monochromatic beam. The results showed that utilizing variations allowed for faster reconstruction of the absorption spectrum compared to the scanning approach, while also achieving higher spectral resolution.

Chapter 3: Experimental details

In the previous chapter, I discussed the motivation behind utilizing GM for imaging, fluorescence, and spectroscopy. In this chapter, I will focus on the practical aspects. I will discuss the reconstruction protocol, experimental setup, and present the main results obtained. For more comprehensive and detailed information, I recommend referring to the articles below.

3.1 Ghost metrology protocol

I will begin by explaining the fundamental protocol that is common to all applications. The single-pixel signal is represented by a vector T, while the different illuminated structures are represented by a matrix A, where each row corresponds to a specific structure. The vector x represents the unknown sample response, and thus the vector T is obtained as the product of the matrix A and the vector x:

$\mathbf{A}\mathbf{x} = \mathbf{T}$

Essentially, this equation forms a linear system. Therefore, if the number of rows in matrix A is equal to or greater than the number of elements in vector x, we can straightforwardly solve this problem. This implies that we need a number of repetitions equal to or greater than the number of pixels in the reconstructed sample. However, by utilizing a sparsity constraint, the equation can be solved using fewer equations than values, thereby reducing the required number of repetitions. This is the underlying principle of compressed sensing, which encompasses various algorithms. In my work, I employed the TVAL algorithm [36], which focuses on sparsity in the variation rather than the signal itself.



Figure 4: The GM experimental setups, depicting the different representations within the basic equation of GM. Although the equation Ax = T remains the same for all experiments, the variables represent different measurements in each case.

All three experiments I conducted can be represented using the same procedure and protocol. However, they are implemented in different domains. Fig. 4 provides a comprehensive representation of each method and its corresponding variables.

3.2 Methods and results

While the GM protocol remains consistent across all experiments, each experiment presents unique challenges and the innovation in the results pertains to specific fields. In this section, I will elucidate the challenges encountered in each experimental setup and highlight the main findings, which are depicted in Figure 5.



Figure 5: Experimental results of x-ray GM. (A) Transmission function showing two slits of sizes 50 and 80 microns reconstructed by x-ray computational ghost imaging. (B) Two-dimensional chemical mapping of Iron and Cobalt thin foils reconstructed using x-ray ghost fluorescence. (C) Absorption spectra of SiC, SiN, and pure Si molecules reconstructed using ghost spectroscopy at XFEL. For more detailed information, please refer to the corresponding papers.

3.2.1 X-ray computational ghost imaging

The first demonstration of x-ray ghost imaging [28] utilized the conventional approach of splitting the beam with a beam splitter and capturing the spatial distribution using a camera. In my experiment I performed the first demonstration of computational GI where the spatial distribution (the matrix A) is calculated by the propagation from fabricated mask. Thus, the splitting and the camera are not required. While computational GI is very easily implemented on the optical regime by a spatial light modulator, these devices are not existing in the x-ray regime. I designed and fabricated a mask with two microns features and I show in the experiment that I can reconstruct a slit of 50 and 70 microns with a resolution of few microns

as presented in figure 5(A). This milestone represents a breakthrough in achieving enhanced resolution through structure illumination in the x-ray regime, where spatial light modulators are not readily available.

3.2.2 X-ray ghost fluorescence

In this experiment, I expanded the application of x-ray GI to fluorescence imaging by detecting the fluorescence radiation instead of measuring the transmission intensity. For each iteration, I measured the total intensity of each emission line (the vector T) and reconstructed each element separately. I demonstrated this approach using a sample containing Iron and Cobalt. After successfully reconstructing each element, I overlapped them, visually representing Iron in red and Cobalt in green as shown in figure 5(B). The significant advantage of this method is the ability to achieve high-quality reconstructions with a reduced number of scanning points compared to traditional raster scanning. I demonstrated that even by using number of iterations that is tenth of the number of pixels, I could reconstruct the sample with a resolution of approximately 30 microns, which can be further improved with better masks. This research opens up new possibilities for advanced imaging techniques, extending the capabilities XRF to various fields, including medical imaging and security applications.

3.2.3 X-ray ghost spectroscopy

In this experiment, I conducted the GM protocol at two different XFEL facilities: FERMI XFEL using XUV radiation, and the Swiss XFEL using hard x-rays. The paper included in this thesis focuses on the results obtained with XUV radiation, while the results from the Swiss XFEL are currently being analyzed. Unlike the previous experiments where the GM protocol operated in the spatial domain, this experiment operates entirely in the spectral domain. The variables A, x, and T represent spectral components.

A significant distinction here is that instead of using a mask to create the structure, the variations are inherent to the XFEL SASE process. One of the main challenges in implementing the GM protocol in this context was dealing with the presence of an envelope in the variations. To ensure accurate results, it is crucial for the variations to be random and devoid of any envelope. To address this challenge, I developed a new protocol detailed in the third paper to effectively clean up the envelope.

In addition to demonstrating the reconstruction of different molecules, I also emphasized the superior performance of ghost spectroscopy compared to other techniques. For the same spectral range, scanning with broadband radiation required 15 steps with a resolution of 500

meV. On the other hand, employing monochromatic radiation necessitated 51 steps, resulting in a resolution of 75 meV. In contrast, using ghost spectroscopy, I achieved spectrum reconstruction with just 15 scanning steps and a resolution of 35 meV. Furthermore, I employed ghost spectroscopy to monitor the spectral response of the sample to optical pumps. In this scenario, the measurement duration is crucial due to the need for repeating the process for each time delay.

Given that most XFELs operate with SASE radiation, we anticipate that our technique will have broad applications in ultrafast-transient absorption measurements at high photon energies.

Chapter 4: Publications

My thesis comprises three publications that detail the three experiments I mentioned above. The first publication focuses on computational ghost imaging, demonstrating the spatial resolution advantage of GM. The second publication, on ghost fluorescence, showcases the additional benefit of using GM to reduce measurement duration for fluorescence imaging. Lastly, the third publication on ghost spectroscopy highlights the use of natural spectral variations at XFEL to overcome the trade-off between resolution and measurement duration in XAS measurements. These three experiments collectively showcase the capabilities and advantages of GM in various imaging and spectroscopy applications.

Article 1-

X-ray computational ghost imaging with singlepixel detector

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X-ray computational ghost imaging with single-pixel detector

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Research Article

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Abstract: We demonstrate computational ghost imaging at X-ray wavelengths with only one single-pixel detector. We show that, by using a known designed mask as a diffuser that induces intensity fluctuations in the probe beam, it is possible to compute the propagation of the electromagnetic field in the absence of the investigated object. We correlate these calculations with the measured data when the object is present in order to reconstruct the images of 50 µm and 80 µm slits. Our results open the possibilities for X-ray high-resolution imaging with partially coherent X-ray sources and can lead to a powerful tool for X-ray threedimensional imaging.

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1. Introduction

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X-ray imaging techniques are widely used in a variety of fields ranging from basic science and high-tech industry to medicine and homeland security. The main advantages of the Xrays are the extremely high spatial resolution, the strong dependence on atom species and densities, and the relatively long penetration depth compared to electrons, which are commonly used for high-resolution imaging.

Despite the existence of many instruments and devices, which are based on X-ray imaging, there are several physical limitations that restrict the resolution and contrast of these techniques. The main fundamental challenge in X-ray imaging is the absence of high quality lenses because of their small magnification and aperture size. It is therefore desired to develop X-ray imaging techniques that do not require lenses and provide high quality images with high resolution and high contrast. Indeed, many techniques and approaches for lensless imaging have been demonstrated with various degree of success [1-5], but none of them has become an ultimate method for imaging. Although some of the techniques have been proven to be very successful in imaging of nanoscale objects [1-4], they require high coherence and therefore are suitable only to synchrotron beamlines with high coherence or to X-ray freeelectron lasers.

Ghost imaging (GI) and ghost diffraction (GD) are imaging techniques that have been proven to be applicable even with low coherence sources [6,7]. They have been investigated mainly in the optical regime [7-22] and recently several very significant publications have demonstrated the effects with X-rays [23-29]. In addition of being methods that can be implemented with incoherent sources, GI and GD can lead to imaging methods with very low dose [28] and to imaging of objects in turbid media [14-16]. The later can lead to imaging of biological samples in their natural environment

In the conventional schemes, GI and GD with partially coherent sources are implemented by introducing fluctuations into the beam by a rotating diffuser and then splitting the beam into two beams with identical intensity fluctuations. One of the beams impinges on the object and is detected by a single-pixel detector while the other beam is detected by a multi-pixel

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detector that is blind to the object. In GI, the single-pixel detector is adjacent to the object while in GD the single-pixel detector is mounted far from the object and the distances between the two detectors to the beam splitter are equal. After making many repetitions (realizations) of the process for different positions of the diffuser, the correlation measurements between the two beams are used to reconstruct either the image in the case of GI or the intensity of the diffraction pattern of the object in case of GD. In another scheme for GI [23,28], a moving diffuser is also used to introduce intensity fluctuations, but the spatial distributions of the intensities at the multi-pixel detector for the various configurations of the diffuser are measured first in the absence of the object. These distributions of the intensity are recorded and then the object is inserted into the beam and a single-pixel detector is used to measure the intensities for the same configurations of the moving diffuser. In the last step, the correlations between the two measurements are computed and used to reconstruct the image. In this scheme the beam splitter is not required, but it is still necessary to use the multi-pixel detector in the first step.

A method that requires only one single-pixel detector and no beam splitters has several important advantages with respect to the other methods and can be used to overcome several of the fundamental challenges in the other approaches. In particular, single-pixel detectors are faster, cheaper, and easier to use than multi-pixel detectors. In the conventional scheme for GI and GD, the beam splitter adds different intensity fluctuations to each of the beams and therefore reduces the signal-to-noise ratio [25]. In addition, it is very challenging to find X-ray beam splitters with equal reflectance and transmission and with negligible loss, thus the contrast of the image is limited [25]. In the other approach without the beam splitter [23,28] the resolution and the field of view are limited by the pixel size and the number of pixels of the multi-pixel detector. These limitations can be lifted by using only one single pixel detector. Another significant advantage of imaging with a single-pixel detectors. This advantage could be extremely important for measurements that require three or more dimensional imaging.

Interestingly, a method that implements GI with only one single-pixel detector, which is known as computational ghost imaging (CGI, or for ghost diffraction CGD), has been proposed theoretically by Shapiro [13] and demonstrated with optical radiation [16–21]. The basic concept is to replace the diffuser with an unknown scatter distribution by a diffuser with a known scatter distribution. Since the phase and amplitude fluctuations that are induced by the diffuser are known, it is possible to use the Fresnel-Huygens propagator to compute the intensity profile at the detector for each of the realizations thus this procedure does not require a multi-pixel detector. In the last step, the calculated intensity distributions are correlated with the measured intensities at the single-pixel detector that is placed behind the object and the image is reconstructed from the computed correlations. In the optical regime the diffuser is typically implemented by using a spatial light modulator (SLM) [17–19] or a digital micro-mirror device [20,21], but at X-ray wavelengths similar devices are not available. Consequently, the implementation of CGI with X-rays requires a different approach.

Here we present the demonstration of CGI with one single-pixel detector at X-ray wavelengths. We design masks, which are based on numerical simulations we performed, and are fabricated by nanotechnology techniques. We demonstrate the imaging of 50 μ m and 80 μ m slits at a resolution of about 10 μ m with two different masks.

2. CGI procedure

The calculation procedure relies on the derivation of CGI by Shapiro [13], but in our procedure we substitute the SLM by a mask made by photolithography. The main difference between the experiment we describe here and the proposal made by Shapiro in [13] is that the source, which impinges upon the mask in our experiment is partially coherent where the

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spatial coherent length is on the order of the speckle size, while Shapiro considered a scenario where the beam that illuminates the SLM is completely coherent. Consequently, we extend the procedure of Shapiro to partially coherent sources as we elaborate below.

Since we know the thickness of the mask at each position, we can calculate the twodimensional transmission function U(x,y) by using the tabulated data for X-ray indices of refraction and absorption coefficients [30]. Here x and y are the coordinates across the mask. The mask pattern is designed so that at each of the realizations, the beam hits a small portion of the mask where the variations are only along the x axis. Therefore, we define the onedimensional transmission function for every realization r as:

$$U_r(x) = B_r(x)e^{i\varphi_r(x)}$$
(1)

Here $\phi_r(x)$ and $B_r(x)$ are the phase that the mask introduces to the beam and the square root of the intensity transmission of the mask, respectively, at each position x. Once we know the electric field after the mask, we can calculate the intensity distribution at the plane of the object, which is at a distance z from the mask, by using the Huygens-Fresnel propagator:

$$I_{C_{r}}(x',z) = \left| \int dx E_{in}(x) U_{r}(x) e^{\frac{ik}{2z}(x-x)^{2}} \right|^{2}$$
(2)

Here $E_{in}(x)$ is the electric field before the mask, k is the wave vector, and x' is the coordinate across the plane of the object.

Since the source is partially coherent we use a model where we express E_{in} as:

$$E_{in}(\mathbf{x}) = \int_{0}^{T_d} dt \, A e^{i(\mathbf{k}\mathbf{x} - \omega t + \phi(\mathbf{x}, t))}$$
(3)

Here A is the field amplitude, ω is the angular frequency, and T_d is the integration time of the detector. $\phi(x, t)$ is a random temporal and spatial phase function, which is extracted according to the Van Cittert-Zernike theorem [31] from a Gaussian distribution such that the two point correlation function is limited by the coherence volume of the field. The spatial coherence length in our experiment can be evaluated by using [31] $\sigma_l \approx \lambda/\theta$ where λ is the wavelength and θ is the divergence angle to be several microns. The temporal coherence length is about a femtosecond and is determined by the bandwidth of the input monochromator.

We denote the transmission function of the object as T(x'). The intensities at the singlepixel detector that is mounted immediately after the object are given by $I_{B_c} = \int dx I_{C_c} T(x') \cdot I_{B_c}$

is cross-correlated with the computed intensity patterns I_{c_r} and after N realizations the image can be reconstructed by using the second-order-intensity correlation function:

$$G(\mathbf{x}) = \frac{1}{N} \sum_{r=1}^{N} \left(\mathbf{I}_{\mathbf{B}_{r}} - \left\langle \mathbf{I}_{\mathbf{B}} \right\rangle \right) \mathbf{I}_{\mathbf{C}_{r}} = \left\langle \mathbf{I}_{\mathbf{B}} \mathbf{I}_{\mathbf{C}} \right\rangle - \left\langle \mathbf{I}_{\mathbf{B}} \right\rangle \left\langle \mathbf{I}_{\mathbf{C}} \right\rangle$$
(4)

The $\langle \cdot \rangle$ indicates an ensemble average over the realizations, where each of the realizations refers to a different position on the mask and therefore represents different intensity and phase fluctuations.

3. Experimental setup

We conducted the experiments described below at beamline B16 of Diamond Light Source [32]. The schematic of the experimental system is shown in Fig. 1(a). The distance between the mask and the object is 100 mm and the detector is mounted immediately behind the



object. We use a monochromatic X-ray beam at 11 keV. The divergence angle is about 0.2 mrad and the relative spectral bandwidth $\Delta E/E$ is about 10^{-4} (achieved by using a Si(111) monochromator). The beam with a spot size of 800 μ m x 200 μ m at full width half maximum (FWHM) hits a selected area of the diffuser and propagates according to the pattern in that specific portion. Next, the beam passes through the object and it is collected by the single-pixel detector, which we mount behind the object.



Fig. 1. (a) Schematic of the computational ghost imaging experimental setup. A diffuser is mounted on linear stages. The beam hits a small portion of the diffuser, then it propagates through the object and is detected by a single-pixel detector mounted as close as possible to the object. (b) An example of an illuminated area of mask 2, which is a random pattern of long rectangles with dimensions of $2 \ \mu m x 0.2 \ \mu m$. The pattern changes only in x axis. (c) Two examples of calculated diffraction patterns for two different realizations.

We measured the intensity at the detector for different positions across the mask. We correlate the measured intensities at the detector with the calculations of the free space propagation by using the procedure described in the previous section.

We test two different masks, for the diffusers, which are produced by direct laser lithography. The masks consist of random patterns of metal rectangles on a glass substrate. These features introduce a phase shift of about 0.05π and absorption of about 2%. The specifications of the two masks are summarized in Table 1. An example of one projection area on the second mask is shown in Fig. 1(b), and two examples of calculated diffraction pattern are shown in Fig. 1(c).

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Mask number	Substrate material	Substrate thickness [µm]	Feature material	Feature thickness [µm]	Minimum feature size [µm]	Mask area [cm ²]
1	Quartz	~1500	Iron oxide	0.26 ± 0.03	1 ± 0.05	~100
2	Quartz	~350	Chromium	0.2 ± 0.02	2 ± 0.2	~78.5

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The objects we measure are 50 μ m and 80 μ m slits, which are implemented by using a one-dimensional motorized slit with a controllable size. The detector is an avalanche photodiode (APD).

We use the ring current of the synchrotron to filter out the slow temporal fluctuations, the decay, and the filling of the synchrotron beam. We measure the beam profile to normalize the image and to filter out spatial noises. The raw measured data include a spatial high frequency noise that we assume is caused mainly by artifacts in the fabrication of the masks. We filter out this noise by applying a low pass filter in the data analysis process.

We perform the measurements for three combinations of different masks and objects as we summarize in Table 2.

Table 2. Parameters of the CGI experiments

Object size [µm]	Mask number	Average counts per realization	Number of realizations	Measured relative intensity fluctuations [%]
50	2	$\sim 7.10^{7}$	$1.8 \cdot 10^{3}$	0.29
80	2	$\sim 1.10^{8}$	$2.3 \cdot 10^{3}$	0.14
80	1	$\sim 4.10^{6}$	$1.8 \cdot 10^{3}$	0.20

4. Results

We first describe the demonstration of CGI with X-rays, which we show in Fig. 2. Figure 2(a) shows the image of a 50 μ m slit that is obtained by using mask 2. We find that the FWHM of the image is 51 μ m ± 10 μ m. Figures 2(b) and 2(c) show images of an 80 μ m slit that is obtained by using mask 2 and mask 1, respectively. We find that the FWHM of the images are 78 μ m ± 10 μ m and 81 μ m ± 8 μ m respectively. The blue dots are CGI results when the distance between the sequential dots is 2 μ m and 1 μ m for mask 2 and for mask 1 respectively.

To test the performance of our measurements we compare the slit widths we measure to the slit sizes we set. The spatial resolution of our measurements is determined by the speckle size at the image plane, which is larger than the feature size at the mask plane because of the diffraction of the speckle pattern over the distance between the diffuser and the plane of the object. The precision of the mask position alignment (about $\pm 2 \mu m$) also affects the resolution. We therefore estimate the resolution of our measurements to be about 10 μm and 8 μm for mask 2 and for mask 1 respectively. In addition, the calibration of the slit, which is not better than 2 microns, introduces additional uncertainties with respect to the expected width and the low pass filter we use in our data analysis also affects the edges of the images. Within these uncertainties, the widths of the slits we measure agree with the widths of the motorized slits that we set. Of importance, we observe the images of the slits only when we use the correct diffuser mask pattern in our calculations of the CGI image.





Fig. 2. Experimental results of computational ghost imaging for (a) a 50 μm slit with mask number 2, (b) an 80 μm slit with mask number 2, and (c) an 80 μm slit with mask number 1. The solid lines are guides for the eye.

5. Dependence on the source coherence properties

The source we use to illuminate the mask is partially coherent in contrast to demonstrations of CGI with optical radiation. This major difference leads to the question of how do the image quality and resolution depend on the spatial coherence length of the source?

To answer this question, we simulate the CGI procedure for a 15-micron slit and compare between several spatial coherence lengths and between two types of diffuser masks: a pure phase mask and a pure amplitude mask. We summarize the results of the comparison in Fig. 3. In the upper row (Figs. 3(a)-3(d)) we show the results for the amplitude mask and in the lower row (Figs. 3(e)-3(h)) we show the results for the phase mask. Since the results depend mainly on the ratio between the coherence length and the features size, we define the ratio R = σ_i/MFS , where the MFS is the minimum feature size.



Fig. 3. CGI simulations for several coherent lengths. R is the ratio between the spatial coherence length and the minimum features size of the diffuser. The object is a 15 μ m slit (the purple lines are the theoretical slit). In panels (a)-(d) the mask is an amplitude mask and in panels (e)-(h) the mask is a phase mask. The propagation distance we use for the simulations is 100 mm.

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The results in Figs. 3(a)-3(d) indicate that the image can be reconstructed even when the coherence length is smaller than the speckle size if the diffuser is an amplitude mask. However, the resolution improves with the coherence length. For coherence lengths that are shorter than the features size as in Fig. 3(a) the sharp edges of the slits are completely blurred. This is because the divergence angle is inversely proportional to the coherence length (as described in section 2). Since the beam that is scattered from the diffuser expands according to the diffraction angle, the larger the diffraction angle the broader the speckles at the object plane and the resolution decreases.

For the phase mask, the image can be reconstructed only if the coherence length is on the order of the speckles size as in Figs. 3(f)-3(h). We note that in the range where the coherence length is equal or slightly shorter than the feature size of the diffuser, the reconstruction depends strongly on the properties of the partial coherent source model.

In our experiment, the diffuser masks introduce mainly amplitude fluctuations into the beam. Therefore, we conclude that the CGI procedure works, although the coherence length is on the order of the speckle size, and it is possible that the contribution of the phase information is very small. The short coherence length in our case mainly leads to blurring and to the reduction of the spatial resolution, as we show in Fig. 3(b).

In addition, we deduce from the results of Fig. 3 that a larger ratio between the coherence length and the mask feature size could lead to the possibility of using the phase contribution from the mask. This conclusion is important for small objects since the amplitude modulation by the mask is limited by the height of the features of the mask, which are limited by the aspect ratio, which is determined by fabrication limitations. Thus, smaller lateral size of the features has smaller amplitude fluctuations and the addition of the phase fluctuations can enhance the contrast of the reconstructed image.

6. Signal-to-noise ratio and image quality

After we demonstrated the CGI effect and discussed its dependence on the spatial coherence length we turn to quantify the signal-to-noise ratio (SNR) and its dependence on the number of realizations. Theoretically the SNR scales as the square root of the ratio between the number of realizations N and the number of speckles transmitted through the object N_s [33,34]: SNR $\propto \sqrt{N/N_s}$. Figure 4 shows the SNR as a function of the number of realizations N for CGI results with the 50 µm slit that we show in Fig. 2(a). The black dots are the experimental results and the blue line is an analytic fitting function $a\sqrt{N}$, where "a" is a constant. The SNR matches approximately to the analytical fit and the value of the parameter "a" is 0.5. This result matches to the order of $1/\sqrt{N_s} \propto 10^{-1}$, when N_s is the spot size divided by the feature size. The analysis of the other two experiments yields similar results.



Fig. 4. The SNR as a function of the number of realizations N for CGI results with the 50 μm slit that we show in Fig. 2(a). The black dots are experimental results and the blue solid line is the analytic fitting function a \sqrt{N} . See details in the text.

While the results shown above demonstrate the feasibility of CGI, the quality of the images can be further improved by increasing the thickness of the speckles and hence the amplitude variations that are induced by the diffuser mask. In addition, since the beam diffracts from the mask plane to the image plane, the distance between the diffuser and the object is one of the properties that determines the spatial resolution. Figure 5(a) shows a comparison for CGI of a 50 μ m slit (the purple line is the theoretical slit) between the experimental results (blue dotted line), a simulation for the experimental parameters (green dashed line). The results in this panel are obtained by assuming that the object is mounted at the same distance of the experiment (100 mm). Figure 5(b) shows the similar simulations with the exception that the distance between the mask and the object is 30 mm. The coherence length for the simulations is 1 μ m.



Fig. 5. Comparison between the CGI experimental results (blue dotted line), CGI simulation with the mask that we used in the experiment (green dashed line), and simulation with an ideal mask modulation (red dashed line) for a 50-µm slit (the purple line is the actual shape of the slit). In panel (a) the distance between the diffuser and the object is 100 mm. In panel (b) the distance is 30 mm.

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It is clear that the results of the simulations with the parameters of the experiment (green dashed line) and the experimental results (blue dotted line) in Fig. 5(a) agree within the experimental resolution. However, there is a distortion in the measured image, which is absent in the simulations. Since the calculations in the CGI procedure are based on the information of the mask pattern, we believe that the distortion is caused by inaccuracies in the mask fabrication process.

We note that the resolution of the simulations and the experimental results in Fig. 5(a) are nearly equal. This similarity suggests that the main reason for the limited resolution is the divergence of the beam, and not the experimental errors. Based on this considerations, we anticipate that it would be possible to improve the spatial resolution significantly by moving the object closer to the diffuser as we can see clearly from Fig. 5(b) where the resolution is improved in both simulations (dashed lines). Equivalent ways to improve the resolution are to increase the R factor by using a source with a larger spatial coherence length or by using a mask with smaller features.

We note that the simulations with the ideal mask (red dashed line) show higher SNR. This suggests that it would be possible to improve the SNR of the image by increasing the thickness of the mask features, which will lead to stronger variations of the amplitudes and the phases and a higher correlation function.

7. Conclusion

We have demonstrated the first experimental observation of CGI at X-ray wavelengths with only one single-pixel detector. The simulations we performed suggest that it is possible to improve the SNR, the contrast, and the spatial resolution of the reconstructed images by optimizing parameters such as the aspect ratio and thickness of the speckle size. These improvements can be achieved by using advanced lithography techniques, such as X-ray photolithography [35].

We note that since it is possible to control the parameters of the diffuser by designing an efficient scatter distribution, CGI can also lead to a reduction in the number of realizations that are required for the reconstruction of the images [18,19] and therefore to either shorter measurement durations or to a lower radiation dose that is required for the reconstruction of the images. Furthermore, our method is not limited to near field imaging. By mounting the object far from the detector it would be possible to measure the diffraction pattern of an object [13,17] and to reconstruct the object by a phase retrieval algorithm [22]. In addition, our technique advances the possibilities for three-dimensional imaging [20,21] and for imaging of objects, which are embedded in liquid [16]. Finally, we note that since our technique does not require either high coherence or high brightness, it can be used not just with synchrotron radiation but also with tabletop X-ray sources.

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Reference

- ī. J. Miao, P. Charalambous, J. Kirz, and D. Sayre, "Extending the methodology of X-ray crystallography to allow
- J. Miao, P. Charatambous, J. Kirz, and D. Sayre, Extending the metodology of A-ray drystanography to anow imaging of micrometre-sized non-crystalline specimens," Nature 400(6742), 342–344 (1999).
 I. McNulty, J. Kirz, C. Jacobsen, E. H. Anderson, M. R. Howells, and D. P. Kern, "High-resolution imaging by Fourier transform X-ray holography," Science 256(5059), 1009–1012 (1992).
 S. Eisebit, J. Lüning, W. F. Scholter, M. Lörgen, O. Hellwig, W. Eberhardt, and J. Stöhr, "Lensless imaging of magnetic nanostructures by X-ray spectro-holography," Nature 432(7019), 885–888 (2004). 2.
- 3.

Optics EXPRESS

Research Article

- P. Thibault, M. Dierolf, A. Menzel, O. Bunk, C. David, and F. Pfeiffer, "High-resolution scanning x-ray 4.
- H. M. Chapman and K. A. Nugent, "Coherent lensless X-ray imaging," Nat. Photonics 4(12), 833–839 (2010). 5.
- J. Cheng and S. Han, "Incoherent coincidence imaging and its applicability in X-ray diffraction," Phys. Rev. Lett. **92**(9), 093903 (2004). 6. 7.
- Y. Cai and S. Y. Zhu, "Ghost imaging with incoherent and partially coherent light radiation," Phys. Rev. E Stat. Y. Cai and S. Y. Zhu, "Ghost imaging with incoherent and partially coherent light radiation," Phys. Rev. E S Nonlin. Soft Matter Phys. 71(5), 056607 (2005).
 R. S. Bennink, S. J. Bentley, and R. W. Boyd, "Two-Photon" coincidence imaging with a classical source," Phys. Rev. Lett. 89(11), 113601 (2002).
 J. H. Shapiro and R. W. Boyd, "The physics of ghost imaging," Quantum Inform. Process. 11(4), 949–993 8.
- 9.
- (2012)10.
- P. Ryczkowski, M. Barbier, A. T. Friberg, J. M. Dudley, and G. Genty, "Ghost imaging in the time domain," Nat. Photonics 10(3), 167-170 (2016).
- P. A. Morris, R. S. Aspden, J. E. Bell, R. W. Boyd, and M. J. Padgett, "Imaging with a small number of photons," Nat. Commun. 6(1), 5913 (2015). 11.
- C. Thiel, T. Bastin, J. Martin, E. Solano, J. von Zanthier, and G. S. Agarwal, "Quantum imaging with incoherent photons," Phys. Rev. Lett. 99(13), 133603 (2007). 12.
- J. H. Shapiro, "Computational ghost imaging," Phys. Rev. A 78(6), 061802 (2008).
 J. Cheng, "Ghost imaging through turbulent atmosphere," Opt. Express 17(10), 7916–7921 (2009) 13.
- 15. R. E. Meyers, K. S. Deacon, and Y. Shih, "Turbulence-free ghost imaging," Appl. Phys. Lett. 98(11), 111115
- (2011). 16. M. Le, G. Wang, H. Zheng, J. Liu, Y. Zhou, and Z. Xu, "Underwater computational ghost imaging," Opt.
- Express **25**(19), 22859–22868 (2017). Y. Bromberg, O. Katz, and Y. Silberberg, "Ghost imaging with a single detector," Phys. Rev. A **79**(5), 053840 17.
- (2009).18. . M. Mahdi Khamoushi, Y. Nosrati, and S. H. Tavassoli, "Sinusoidal ghost imaging," Opt. Lett. 40(15), 3452-
- 3455 (2015).
- 3455 (2015).
 W. Chen and X. Chen, "Object authentication in computational ghost imaging with the realizations less than 5% of Nyquist limit," Opt. Lett. 38(4), 546–548 (2013).
 B. Sun, M. P. Edgar, R. Bowman, L. E. Vittert, S. Welsh, A. Bowman, and M. J. Padgett, "3D computational imaging with single-pixel detectors," Science 340(6134), 844–847 (2013).
 Z. Zhang, S. Liu, J. Peng, M. Yao, G. Zheng, and J. Zhong, "Simultaneous spatial, spectral, and 3D compressive imaging via efficient Fourier single-pixel measurements," Optica 5(3), 315–319 (2018).
 R. Borghi, F. Gori, and M. Santarsiero, "Phase and amplitude retrieval in ghost diffraction from field-correlation reconstruct," *Burg Lett* 6(12), 127001 (2006).

- K. Borgin, F. Oor, and M. Sandarstero, Phase and amplitude refreval in globs diffraction from field-correlation measurements," Phys. Rev. Lett. **96**(18), 183901 (2006).
 H. Yu, R. Lu, S. Han, H. Xie, G. Du, T. Xiao, and D. Zhu, "Fourier-transform ghost imaging with hard X rays" Phys. Rev. Lett. **117**(11), 113901 (2016).
 D. Pelliccia, A. Rack, M. Scheel, V. Cantelli, and D. M. Paganin, "Experimental x-ray ghost imaging," Phys. Rev. Lett. **117**(11), 113902 (2016).
- Rev. Lett. 117(11), 115902 (2016).
 D. Pelliccia, M. P. Olbinado, A. Rack, A. M. Kingston, G. R. Myers, and D. M. Paganin, "Towards a practical implementation of X-ray ghost imaging with synchrotron light," IUCrJ 5(4), 428–438 (2018).
 A. M. Kingston, D. Pelliccia, A. Rack, M. P. Olbinado, Y. Cheng, G. R. Myers, and D. M. Paganin, "Ghost tomography," Optica 5(12), 1516–1520 (2018).
 A. Schori and S. Shwartz, "X-ray ghost imaging with a laboratory source," Opt. Express 25(13), 14822–14828 (2017). 25.
- 26. 27.
- (2017). 28. A.-X. Zhang, Y.-H. He, L.-A. Wu, L.-M. Chen, and B.-B. Wang, "Tabletop x-ray ghost imaging with ultra-low
- radiation," Optica 5(4), 374–377 (2018). A. Schori, D. Borodin, K. Tamasaku, and S. Shwartz, "Ghost imaging with paired x-ray photons," Phys. Rev. A 29.
- (Coll Park) 97(6) 063804 (2018)
- (Coll. Park) 97(6), 063804 (2018).
 30. B. L. Henke, E. M. Gullikson, and J. C. Davis, "X-ray interactions: photoabsorption, scattering, transmission, and reflection at E= 50-30,000 eV, Z= 1-92," Atom. data Nucl. data 54(2), 181–342 (1993).
 31. J. W. Goodman, *Statistical optics* (Wiley classics library, 2000), Chap. 5.
 32. K. J. S. Sawhney, I. P. Dolbnya, M. K. Tiwari, L. Alianelli, S. M. Scott, G. M. Precce, U. K. Pedersen, and R. D. Walton, "A test beamline on diamond light source," in Proceedings of AIP (2010, June), pp. 387–390.
 33. B. I. Erkmen and J. H. Shapiro, "Signal-to-noise ratio of Gaussian-state ghost imaging," Phys. Rev. A 79(2), 032832 (2000).

- 023833 (2009). 34.
- 35.
- 023833 (2009).
 D. Ceddia and D. M. Paganin, "Random-matrix bases, ghost imaging, and x-ray phase contrast computational ghost imaging," Phys. Rev. A (Coll. Park) **97**(6), 062119 (2018).
 C. Xue, J. Zhao, Y. Wu, H. Yu, S. Yang, L. Wang, W. Zhao, Q. Wu, Z. Zhu, B. Liu, X. Zhang, W. Zhou, and R. Tai, "Fabrication of large-area high-aspect-ratio periodic nanostructures on various substrates by soft X-ray interference lithography," Appl. Surf. Sci. **425**, 553–557 (2017).

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Article 2-

Chemical element mapping by x-ray computational ghost fluorescence

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Chemical element mapping by x-ray computational ghost fluorescence

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Chemical element mapping is an imaging tool that provides essential information about composite materials, and it is crucial for a broad range of fields ranging from fundamental science to numerous applications. Methods that exploit x-ray fluorescence are very advantageous and are widely used, but require focusing of the input beam and raster scanning of the sample. Thus, the methods are slow and exhibit limited resolution due to focusing challenges. Here, we demonstrate an x-ray fluorescence method based on computational ghost imaging that overcomes those limitations since it does not require focusing and show that when it is combined with compressed sensing the total measurement time can be significantly reduced. Our method opens the possibility to significantly enhance the resolution of chemical element maps and to extend the applicability of x-ray fluorescence inspection to new fields where the measurement time is a critical parameter. © 2022 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

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1. INTRODUCTION

x-ray fluorescence (XRF) is a powerful method to identify and map the chemical compositions of samples with intriguing applications that are exploited in a broad range of fields from fundamental science to industry and cultural heritage. Examples for scientific disciplines where XRF plays a prominent role include materials science, electrochemistry [1], biology [2], paleontology [3], and archaeology [4]. Industrial applications include, for example, metal analyzers for small parts that are produced by the automotive and aerospace industries [5]. In cultural heritage, XRF is very useful in providing information on the hidden layers of famous paintings [6].

The basic principle of XRF is simple and is based on the x-ray fluorescence process in which x-ray radiation is used to excite core electrons in the sample. When the core electrons are excited or ejected from the inner shells of the atoms, holes are formed in those shells. The electrons can return to their ground state or outer electrons can fill the holes leading to the emission of x-ray radiation at photon energies that correspond to the characteristic atomic lines. The spectrum of the emitted radiation (the fluorescence spectrum) is detected and analyzed, and since each chemical element has unique emission lines, the fluorescence spectrum is used to characterize the elemental composition of the sample. The detection can be done by energy-resolving detectors that are simple to use and available components with sufficient energy resolution.

In its simplest form, XRF provides no spatial information since the detector collects the radiation from large areas; in recent decades, however, spatially resolved XRF techniques have been developed and their advent opens appealing opportunities in many fields [1,3,4,6]. However, the main challenge for spatially resolved

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XRF measurements is that, in contrast to transmission measurements, the fluorescence is nondirectional, which means that the application of pixelated detectors is a great challenge. Instead, in most cases, 2D chemical maps are reconstructed by focusing the impinging beam and raster-scanning the sample. With this procedure, the spatial information is retrieved since at each measurement point only a small portion of the sample is irradiated and the resolution is determined by the spot size of the input beam [7]. When the spot size is on the order of several microns, the method is called micro-XRF. Extensions to 3D are also possible by either computed tomography [8,9] or confocal x-ray microscopy [10,11].

Despite being very successful and widely used, XRF faces two major challenges that hamper its performance and the extension of its applicability to further disciplines: (1) focusing of x-ray radiation is difficult, especially at high photon energies, so the ability to use small spot sizes in a broad photon energy range is unique to very few synchrotron beamlines and x-ray free electron lasers [7]. To date, the highest resolution achieved with tabletop sources is several microns [12]. However, it is achievable only in a very limited range of photon energies and at the expense of a significant loss of the input flux. (2) In almost all practical implementations of micro-XRF, the spatial information is obtained by raster scanning. This is a very slow process since the scan is done over every point of sample. For large samples and for 3D imaging, the measurement time is several days.

We note reports on several methods for full-field XRF, which are implemented by photon-energy-resolving pixelated detectors, with capabilities to provide 2D chemical maps in a single frame [13-16]. These techniques are performed by using either simple [13,16] or coded [14,15] apertures in front of the pixelated

detector to address the challenge of the blurring due to the nondirectionality of the fluorescence. However, the spatial resolution and the field of view (for a fixed number of pixels) are limited [13–15]. In addition, because the quantum efficiency of the detectors drops very quickly at photon energies higher than 20 keV, there are inflexible constraints on the distance between the sample and the detector, and the measurements cannot provide 3D information without additional lenses [16], which introduces severe challenges. Another approach to reduce the duration of the XRF measurements is based on scanning procedures [17,18] and information that is obtained from the sample during the scan to improve the scanning effcieny [19]. This is a very interesting direction, but the setup is different and the focusing of the input x-ray beam is still required.

Here, we propose and demonstrate a proof-of-principle experiment for what we believe, to the best of our knowledge, is a new and fast, XRF approach with potentially high spatial resolution that solves those challenges by using structured illumination and correlation. The main advantages of our approach are that it does not require focusing and that the measurement time can be significantly reduced by using compressed sensing (CS) or artificial intelligence (AI) algorithms since our method requires a significantly smaller number of measurement points compared to standard techniques.

Our approach that we denote as x-ray computational ghost fluorescence (GF) is related to the computational ghost imaging (GI) approach proposed by Shapiro in 2008 [20]. While the initial motivation of the computational GI approach was to show that quantum correlations are not essential for GI, it evolved to many interesting directions with intriguing potential applications and has been investigated extensively in a broad range of wavelengths [20-35] from radio waves [23] to X-rays [26,29-32], and even with neutrons [36], and electrons [37]. Computational GI can be used to reconstruct 2D and 3D images [28] and, by using CS [35] or AI [22], the measurement time can be significantly reduced. While several schemes for GI have been demonstrated with X-rays [26,29-32,38-41], in the present work we replace the measurement of the transmission or reflection of the object by the measurement of the x-ray fluorescence, which carries the information on the chemical elements; hence, we can use it for chemical mapping.

We note that the GI approach has been used in the visible range for the measurement of the fluorescence [27,33,34]. However, long wavelength fluorescence measurements are not element specific and, in contrast to our method, cannot be used for chemical element mapping. Moreover, the implementation of GI for XRF, where the main alternative is raster scanning, expresses the strengths of the GI approach, which are the ability to provide spatial information without lenses or mirrors and the natural suitability for compressive measurements, which can be used to reduce the measurement time [42].

2. IMAGE RECONSTRUCTION PROCEDURE

Our procedure relies on a two-step approach for the implementation of computational GI [32]. A flowchart that illustrates the procedure is shown in Fig. 1(a). In both steps, the x-ray beam irradiates a mask with inhomogeneous transmission that induces intensity fluctuations in the beam. The goal of Step I is to measure the intensity fluctuations that the mask introduces at the plane of the sample for each of the realizations that we use in Step II. As we illustrate in Fig. 1(b), this is done in the absence of the object and by mounting a pixelated detector at the plane at which we mount the object in Step II. In Step II, which is depicted in Fig. 1(c), we remove the pixelated detector, insert the object, scan the mask at the same positions as in Step I, and measure the x-ray fluorescence with two photon-energy-resolving silicon drift detectors (SDDs) located at two different positions, as shown in Fig. 1(c). We denote the detector that is located upstream the sample as detector Rand the detector located downstream from the sample as detector T. We use two detectors to show that the chemical map can be reconstructed by mounting the detector at any direction around the sample and each of the maps is reconstructed using the data from a single SDD.

After completing the measurements for the entire set of realizations, we obtained two sets of data. One contains the patterns of the mask (measured in Step I) and the other contains the corresponding intensities for each of the fluorescence emission lines (measured in Step II). To reconstruct each shape of the emitters, we separately exploit the following reconstruction procedure for each chemical element. We represent the spatial distribution of each chemical element by a vector **x**. Another vector **T**, which includes *n* realizations, represents the intensities of the corresponding emission lines measured by the each of the SDDs. The mask patterns are represented by the matrix **A**, for which every row is a single realization. The vector **T** is equal to the product of the matrix **A** and the vector **x**:

(1)

To find the vector \mathbf{x} with a minimal number of realizations, and consequently to reduce the measurement time, we used the CS approach, which uses a priori knowledge on the structure of the image. We used the protocol of "total variation minimization by augmented Lagrangian and alternating direction algorithms" (TVAL3) [43]. The basic concept of the protocol is that the gradient of many objects in nature can be represented by a sparse matrix. For each chemical element, the vector \mathbf{x} is reconstructed by minimizing the augmented Lagrangian:

Ax = 1

$$\min_{\mathbf{x}} \sum_{i=1}^{m} \|D_i \mathbf{x}\|_2 + \frac{\mu}{2} \|\mathbf{A}\mathbf{x} - \mathbf{T}\|_2^2 \text{ s.t } \mathbf{x} \ge 0,$$
(2)

with respect to the L₂ norm. Here, $D_i \mathbf{x}$ is the *i*th component of the discrete gradient of the vector \mathbf{x} , and μ is the penalty parameter of the model. Here, we set $\mu = 2^9$). After we reconstruct the image for each of the chemical elements, we overlay the images to reconstruct the chemical element map.

3. RESULTS

The source we used in this experiment was a rotating copper anode and the mask was a sandpaper with an average feature size of about 40 μm . Since we used a collimator before the mask, the intensity patterns we measured in Step I [see Fig. 2(a)] are proportional to the spatial variations of the transmission of the mask. Similar to GI, the spatial resolution of our method is determined by the width of the autocorrelation function of the mask that modulates the input x-ray beam [44]. The autocorrelation function of the mask is presented in Fig. 2(b), while the 1D horizontal and vertical projections are presented in Figs. 2(c) and 2(d), respectively. The autocorrelation function are presented in Figs. 2(c) and 2(d), respectively. The autocorrelation function function



Fig. 1. Image reconstruction procedure and schematics of the experimental setup. (a) Flowchart of the reconstruction procedure. In Step I, we measure the intensity patterns induced by the mask in the absence of the object. In Step II we measure the fluorescence from the object. Schematics of the experimental setup for Steps I and II are shown in (b) and (c), respectively.

curve are 33 \pm 7 μm and 31 \pm 7 μm for the horizontal and vertical axes, respectively.

The object we imaged contains three small pieces of iron, cobalt, and brass (Cu_3Zn_2). The direct image and the fluorescence spectrum of the objects are shown in Figs. 2(e) and 2(f), respectively.

Our method can provide the chemical map by mounting the detectors at any position around the sample and at any distance as long as they collect the fluorescence as emitted from the sample. To display this ability, we present the images reconstructed by our method for the iron and cobalt objects in Figs. 3(a) and 3(b) for detector R and detector T, respectively. The images were reconstructed using 550 realizations and the CS procedure described above. The agreement of the chemical element maps we reconstructed with the real arrangement and structures of the iron and cobalt objects is excellent and indicates the reliability of our method. The resolution of our method is clearly much higher than the spot size of our experiment that was about 1.5 mm, and we

were able to resolve the iron and cobalt objects that are separated by a gap of less than 200 μ m. In addition, we show very clearly that our method can be used to eliminate strong background noise. The images of the iron and cobalt objects are very clear, despite the strong background. Note that the copper emission lines in Fig. 2(f) are stronger than the emission lines of the iron and the cobalt by about a factor of 7. The brass object, however, could not be reconstructed because of the proximity of its emission lines to the emission lines of the radiation of our source.

After successfully showing the ability to reconstruct chemical maps with our method, we then demonstrate that we can use CS to reduce number of realizations; hence, to reduce the measurement time. To quantify the image quality of the reconstructed chemical maps we calculated the peak SNR (PSNR) as a function of the number of realizations. We plot the PSNR of the reconstructed chemical maps we measured with detector T as a function of the number of realizations in Fig. 4. The chemical maps for various compression ratios (CR) are displayed next to the graph. The CR is



Fig. 2. (a) Example of the reference data (the intensity fluctuations induced by the mask). (b) Autocorrelation function of the intensity pattern induced by the mask averaged over all realizations. The blue and green lines indicate the horizontal and vertical cross sections shown in (c) and (d). The blue and green dots are the measured data for the horizontal and vertical cross sections, respectively, and the red curves are interpolation functions. In (e) and (f) normalized direct image and fluorescence spectrum of the object, which consists of iron, coblt, and brass objects are shown. The red line is the spectrum in the absence of the sample and the blue line is the spectrum when the sample is present. The emission lines are indicted near each of the peaks.



Fig. 3. Reconstructed chemical element maps by x-ray GF using (a) detector R and (b) detector T. The red and green areas indicate the areas containing the iron and cobalt elements, respectively.

defined by the number of pixels in the map divided by the number of realizations we used for the reconstruction [37]. The PSNR is calculated by

$$PSNR = 10 \log \left(\frac{peakval^2}{MSE}\right),$$
(3)

where peakval is the maximum possible pixel value of the image and MSE is the mean square error between the reconstructed image and the direct image [Fig. 2(c)]. We calculated the joint PSNR of the cobalt and the iron images as the average between the PSNR values of the images.

The maps we describe in the present work contain 1010 pixels, which is also the number of sampling points if we were using standard micro-XRF. Consequently, the CR expresses the reduction of the measurement time that our method provides. With our technique, we can see a clear image even after 144 realizations, which corresponds to a CR of 7 and identify the objects even with a CR of 20. The important consequence of this result is that with our method, the chemical maps can be measured in much shorter



Fig. 4. PSNR of the reconstructed GF image measured with detector T as a function of the number of realizations. The compressive chemical element maps for various compression ratio (CR) values are displayed near the corresponding points.

times compared to standard micro-XRF methods since the number of realizations with our method is smaller than the number of sampling points with standard XRF methods.

4. **DISCUSSION**

We now discuss several important properties and implications of our method and begin with the spatial resolution. To evaluate the performance of the method and its potential to reconstruct high-spatial resolution chemical maps, we need to compare the resolutions of the reconstructed maps with the resolution of the



Fig. 5. Comparison of the resolutions of the chemical map and the direct image. Description of the edge cross sections for the (a) direct image and (b) chemical map. (c) and (d) Normalized intensity as a function of the position for cross sections I and II, respectively. The blue and magenta dots are the transmission and GF image values, respectively.

direct image of the objects and with the theoretical prediction for GF based on the measured autocorrelation function of the mask.

Since the sample we investigated includes objects with sharp edges, it is possible to estimate the resolution from the smearing of the edges. We estimate the widths of the slopes of the cross sections of the selected regions near the edges in the chemical map and compare them to the corresponding widths of the same objects in the direct image, as shown in Fig. 5. In Figs. 5(a) and 5(b), we describe the selections of the two cross sections (I and II) that are displayed for the chemical map and for the direct image, respectively. In Figs. 5(c) and 5(d), we plot the cross sections I and II, respectively. To compare to the FWHM of the correlation function, we estimated the half width of the slope of the cross sections. For the two edges presented in Fig. 5, we found that the widths of the slopes for the chemical map are 35 \pm 7 μm and 31 \pm 7 μm for cross sections I and II, respectively, and the corresponding widths for the direct images are 19 \pm 7 μm and 12 \pm 7 $\mu m.$ The difference between the resolutions of the GF and the direct image exists since the resolution of GF is determined by the correlation function length of the mask, and is about 30 µm, as we discussed above. The resolution of the direct image, however, is determined by the resolution of the pixelated detector, which is about 15 μ m. Similar results are obtained for the widths of the other edges and they are comparable, as expected, to the width of the autocorrelation function of the mask discussed above.

The resolution we demonstrated in this work is much higher than the spot size we used, which was about 1.5 mm, and it is limited by the feature sizes of the mask we used. The implication is that our method can be used for high-resolution chemical mapping at resolutions that are not limited by the focusing capabilities of a system. It is possible to improve the resolution of our method using masks with smaller features. Recent work shows x-ray GI reconstructions with resolutions below 10 μm using masks that were fabricated by photolithography [26,29,31] or by electroplating [26,31]. The same masks can be used for x-ray GF. Importantly, it is possible to fabricate masks with submicron features using nanotechnology techniques like e-beam lithography and x-ray photolithography. Since the feature size essentially is the parameter that controls that resolution of our method, it opens the possibility for submicron resolution XRF with tabletop sources.

Next, we consider the impact of the CS and the intensity fluctuation magnitude on the image quality since we are interested in the reduction of the measurement time with respect to standard XRF methods, but without deteriorating the image quality. While a high CR can lead to significant reduction in the measurement time it may reduce the image quality and, as we show below, the quality also depends on the magnitude of the intensity fluctuations. Because the image quality in GI methods is determined by the ratio between the variations of the detected intensities for the different realizations to the noise, we define the fluctuation-to-noise ratio (FNR) as

$$FNR = \frac{\text{std}(s)}{\langle \sqrt{s} \rangle},\tag{4}$$

where s is the set of the intensities detected at a specific emission line during entire measurement, $\langle \cdot \rangle$ is the average over all realizations, and std is the standard deviation.

We simulated the experiment and calculated the PSNR of the reconstructed cobalt and iron images as function of the FNR for various CRs. In Fig. 6, we show the results of our simulations. The solid lines are the corresponding fitting curves that we added as guides for the eye. From the results presented in Fig. 6, we see that for FNRs below 1, the PSNR is very small. These values indicate, as

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expected, that no clear image can be reconstructed for FNR values below 1. As the FNR increases, the image quality improves until the value is about 5. At higher FNR values, the image quality is nearly independent from the FNR for any CS value.

For the parameters in our experiment, the FNR values are 3.4 and 4.8 for the cobalt and iron objects, respectively, and the average is 4.1. Accordingly, the PSNR is about 23 for the CR of 2, as shown in Fig. 4. The simulations also explain why we could reconstruct the iron and cobalt, but not the brass object. The brass contains copper and zinc with emission lines very close to the characteristic emission lines of our source, as can be clearly seen in Fig. 2(f), which suggests that the data are noisy for brass. However, it is still possible to resolve the zinc K_{α} line, which might indicate the possibility to reconstruct the brass with standard XRF methods. The FNR, however, is only 1.8, which prevents the reconstruction by GF. This can be overcome in the future by choosing well-separated emission lines or by increasing the depth of the mask features.

From Fig. 6 and the discussion above, it is clear that the reconstruction quality depends on the FNR and the CR. We still, however, need to discuss the impact of the FNR on the reduction of the measurement time and to compare it to the raster scan XRF. In this work, we demonstrated a reduction of the measurement time as the result of reducing the number of scanning points, which is enabled by CS. To understand the reduction in the measurement time compared to standard XRF measurements, we recall that for standard XRF the measurement time is limited by the requirement for sufficient SNR; thus, it depends on the flux of the radiation that irradiates the sample. Since the FNR cannot exceed the SNR, the measurement time of GF will not be shorter than the measurement time of standard methods unless a priori knowledge on the object is used. However, in most cases, there is a priori information such as the sparsity of the object that is used for the application of CS. It is used to reduce the measurement time of GF, as we demonstrated in the present work. Therefore, the measurement time with GF would be shorter than standard methods if the gain using a priori knowledge is larger than the deterioration of the image quality caused by the difference between the SNR and the FNR [42,45,46]. It is clear that when the measurement duration per measurement point (a single sample position for raster scan and a single realization for GF) is not limited by the shot noise (for example, when the motor speed is the limitation), our approach is advantageous, since both the SNR and the FNR can be very high. Hence, the application of CS reduces the number of measurement points and therefore the measurement time.

Finally, we note that since the aspect ratio of the mask features is limited by fabrication or by physical constraints and since the lateral size of the mask features controls the spatial resolution, there is a tradeoff between the resolution and the FNR. This constraint has an important impact on the image quality and on the ability to reduce the measurement time.

5. CONCLUSION

Our work opens the possibility to develop a fast high-resolution chemical element mapping technique without focusing and without moving the sample. In addition to a reduced cost and improved mechanical stability, our method has several advantages over standard methods, which includes a smaller number of sampling points and the applicability for a broad range of photon energies. Further generalization of our results will lead to new applications to extend the capabilities and the impact of XRF to new areas. Medical imaging, for example, can benefit from our method because it is performed at photon energies where lenses are not practical and where the low contrast between various tissues is the main challenge. Today, to improve the visibility and quality of images of soft tissues, contrast agents are used since their transmission contrast is higher than the transmission contrast between different types of soft tissues. However, even with the contrast agents, the visibility is limited. A potential further development of our method is for the measurement the fluorescence from the same contrast agents as a complementary or a completely new modality that could increase the quality of the images or alternatively reduce the dose of the measurements since the fluorescence contrast is significantly higher than the transmission contrast. Another example is for full body scanners used for national security applications. Since our method can provide element-specific images and can be tuned to be blind to human tissues, it can be used to improve the privacy protection of inspected passengers in contrast to other x-ray modalities. Finally, we point out that it is possible to replace the input x-ray beam with an electron beam to excite the inner

shell electrons [47]. In this case, spatial resolutions that exceeds the nanometer scale are feasible and, with our method, it will be possible to significantly reduce the scanning duration.

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Supplemental document. See Supplement 1 for supporting content.

REFERENCES

- 1. J. Lim, Y. Li, D. H. Alsem, H. So, S. C. Lee, P. Bai, D. A. Cogswell, X. Liu, N. Jin, Y. Yu, N. J. Salmon, D. A. Shapiro, M. Z. Bazant, T. Tyliszczak, and W. C. Chueh, "Origin and hysteresis of lithium compositional spatiodynamics within battery primary particles," Science 353, 566–571 (2016). 2. A. Cvetkovic, A. L. Menon, M. P. Thorgersen, J. W. Scott, F. L. Poole,
- II., F. E. Jenney, Jr., W. A. Lancaster, J. L. Praissman, S. Shanmukh, B. J. Vaccaro, S. A. Trauger, E. Kalisiak, J. V. Apon, G. Siuzdak, S. M. Yannone, J. A. Tainer, and M. W. W. Adams, "Microbial metal-loproteomes are largely uncharacterized," Nature 466, 779-782 (2010).
- 3. R. A. Wogelius, P. L. Manning, H. E. Barden, N. P. Edwards, S. M. Webb, W. I. Sellers, K. G. Taylor, P. L. Larson, P. Dodson, H. You, L. Da-Qing, and U. Bergmann, "Trace metals as biomarkers for eumelanin pigment in the fossil record," Science 333, 1622–1626 (2011). 4. A. C. Allwood, M. T. Rosing, D. T. Flannery, J. A. Hurowitz, and C. M.
- Heirwegh, "Reassessing evidence of life in 3,700-million-year-old rocks of Greenland," Nature 563, 241–244 (2018).
- 5. SPECTRO Analytical Instruments GmbH, "High-precision analysis of small parts for aerospace and automotive applications, "https:// extranet.spectro.com/-/media/21264D4E-0D97-490B-996F-9E3C59C ADBE6.pdf.
- 6. R. Ploeger and A. Shugar, "Where science meets art," Science 354, 826-828 (2016).
- 7. G. E. Ice, J. D. Budai, and J. W. L. Pang, "The race to x-ray microbeam and nanobeam science," Science 334, 1234-1239 (2011).
- 8. B. Golosio, A. Simionovici, A. Somogyi, L. Lemelle, M. Chukalina, and A. Brunetti, "Internal elemental microanalysis combining x-ray fluoscence, Compton and transmission tomography," J. Appl. Phys. 94, 145-156 (2003).
- 9. S. A. Kim, T. Punshon, A. Lanzirotti, L. Li, J. M. Alonso, J. R. Ecker, J. Kaplan, and M. Lou Guerinot, "Localization of iron in arabidopsis ed requires the vacuolar membrane transporter VIT1," Science 314, 1295-1298 (2006).
- 10. S. Bauters, P. Tack, J. H. Rudloff-Grund, D. Banerjee, A. Longo, B. Vekemans, W. Bras, F. E. Brenker, R. van Silfhout, and L. Vinoze, "Polycapillary optics based confocal micro x-ray fluorescence and x-ray absorption spectroscopy setup at the European synchrotron radiation facility collaborative research group Dutch-Belgian beamline, BM26A," Anal. Chem. 90, 2389-2394 (2018).
- 11. G. Chen, S. Chu, T. Sun, X. Sun, L. Zheng, P. An, J. Zhu, S. Wu, Y. Du, and J. Zhang, "Confocal depth-resolved fluorescence micro-x-ray absorption spectroscopy for the study of cultural heritage materials: a new mobile endstation at the Beijing Synchrotron Radiation Facility," J. Synchrotron Radiat. **24**, 1000–1005 (2017).
- 12. K. Tsuji, T. Matsuno, Y. Takimoto, M. Yamanashi, N. Kometani, Y. C. Sasaki, T. Hasegawa, S. Kato, T. Yamada, T. Shoji, and N. Kawahara, "New developments of x-ray fluorescence imaging techniques in laboratory," Spectrochim. Acta B At. Spectrosc. **113**, 43–53 (2015).
- G. Xiong, W. Jia, Q. Shan, X. Zhang, X. Tang, and J. Li, "Equipment design and performance characterization of full field x-ray fluorescence (FF-XRF) element distribution imaging system with combined collimating lens (CCL)," Rev. Sci. Instrum. 91, 123701 (2020).
- A. Kulow, A. G. Buzanich, U. Reinholz, C. Streli, and M. Radtke, "On the way to full-field x-ray fluorescence spectroscopy imaging with coded apertures," J. Anal. At. Spectrom. 35, 347-356 (2020).

- 15. A. Haboub, A. A. MacDowell, S. Marchesini, and D. Y. Parkinson, "Coded aperture imaging for fluorescent x-rays," Rev. Sci. Instrum 85, 063704 (2014).
- B. De Samber, O. Scharf, G. Buzanich, J. Garrevoet, P. Tack, M. Radtke, H. Riesemeier, U. Reinholz, R. Evens, K. De Schamphelaere, G. Falkenberg, C. Janssen, and L. Vincze, "Three-dimensional x-ray fluorescence imaging modes for biological specimens using a full-field energy dispersive CCD camera," J. Anal. At. Spectrom. 34, 2083-2093 (2019).
- 17. J. R. Betterton, D. Ratner, S. Webb, and M. Kochenderfer, "Reinforcement learning for adaptive illumination with x-rays," in Proceedings-IEEE International Conference on Robotics and Automation (2020).
- K. Hwang, Y. H. Seo, J. Ahn, P. Kim, and K. H. Jeong, "Frequency selec-tion rule for high definition and high frame rate Lissajous scanning," Sci. Rep. 7, 14075 (2017).
- 19. M. M. Noack, K. G. Yager, M. Fukuto, G. S. Doerk, R. Li, and J. A Sethian, "A Kriging-based approach to autonomous experimentation with applications to x-ray scattering," Sci. Rep. 9, 11809 (2019).
- 20. J. H. Shapiro, "Computational ghost imaging," Phys. Rev. A 78, 061802 (2008)
- 21, G. M. Gibson, S. D. Johnson, and M. J. Padgett, "Single-pixel imaging G. M. Gibson, S. D. Johnson, and M. J. Padgett, "Single-pixel imaging 12 years on: a review," Opt. Express 28, 28190–28208 (2020).
 M. Lyu, W. Wang, H. Wang, H. Wang, G. Li, N. Chen, and G. Situ, "Deep-learning-based ghost imaging," Sci. Rep. 7, 17865 (2017).
 R. Baraniuk and P. Steeghs, "Compressive radar imaging," in *IEEE Radar*
- Conference (IEEE, 2007), pp. 128–133.
- H.-C. Liu and S. Zhang, "Computational ghost imaging of hot objects in long-wave infrared range," Appl. Phys. Lett. **111**, 031110 (2017).
 D. Shrekenhamer, C. M. Watts, and W. J. Padilla, "Terahertz single pixel
- imaging with an optically controlled dynamic spatial light modulator, Opt. Express **21**, 12507–12518 (2013).
- Y. H. He, A. X. Zhang, M. F. Li, Y. Y. Huang, B. G. Quan, D. Z. Li, L. A. Wu, and L. M. Chen, "High-resolution sub-sampling incoherent x-ray imaging with a single-pixel detector," APL Photon. 5, 056102 (2020). 27. V. Studer, J. Bobin, M. Chahid, H. S. Mousavi, E. Candes, and M. Dahan,
- "Compressive fluorescence microscopy for biological and hyperspectral imaging," Proc. Natl. Acad. Sci. USA **109**, E1679–E1687 (2012).
- B. Sun, M. P. Edgar, R. Bowman, L. E. Vittert, S. Welsh, A. Bowman, and M. J. Padgett, "3D computational imaging with single-pixel detectors," ence 340, 844-847 (2013).
- 29. Y. Klein, A. Schori, I. P. Dolbnya, K. Sawhney, and S. Shwartz, "X-ray computational ghost imaging with single-pixel detector," Opt. Expr 27, 3284-3293 (2019).
- O. Sefi, Y. Klein, E. Strizhevsky, I. P. Dolbnya, and S. Shwartz, "X-ray imaging of fast dynamics with single-pixel detector," Opt. Express 28, 24568-24576 (2020).
- Y.-H. He, A.-X. Zhang, W.-K. Yu, L.-M. Chen, and L.-A. Wu, "Energy-selective x-ray ghost imaging," Chin. Phys. Lett. 37, 044208 (2020)
- 32, A.-X. Zhang, Y.-H. He, L.-A. Wu, L.-M. Chen, and B.-B. Wang, "Tabletop x-ray ghost imaging with ultra-low radiation," Optica 5, 374–377 (2018).
 33. S. Ota, R. Horisaki, Y. Kawamura, M. Ugawa, I. Sato, K. Hashimoto, R.
- Kamesawa, K. Setoyama, S. Yamaguchi, K. Fujiu, K. Waki, and H. Noji, "Ghost cytometry," Science **360**, 1246–1251 (2018).
- N. Tian, Q. Guo, A. Wang, D. Xu, and L. Fu, "Fluorescence g with pseudothermal light," Opt. Lett. 36, 3302–3304 (2011). e ghost imaging
- O. Katz, Y. Bromberg, and Y. Silberberg, "Compressive ghost imaging," Appl. Phys. Lett. 95, 131110 (2009).
- A. M. Kingston, G. R. Myers, D. Pelliccia, F. Salvemini, J. J. Bevitt, U. Garbe, and D. M. Paganin, "Neutron ghost imaging," Phys. Rev. A 101, 053844 (2020). 37. S. Li, F. Cropp, K. Kabra, T. J. Lane, G. Wetzstein, P. Musumeci, and D.
- Ratner, "Electron ghost imaging," Phys. Rev. Lett. **121**, 114801 (2018). 38. D. Pelliccia, A. Rack, M. Scheel, V. Cantelli, and D. M. Paganin,
- "Experimental x-ray ghost imaging," Phys. Rev. Lett. 117, 113902 (2016).
- A. Schori and S. Shwartz, "X-ray ghost imaging with a laboratory source," Opt. Express 25, 14822–14828 (2017).
- H. Yu, R. Lu, S. Han, H. Xie, G. Du, T. Xiao, and D. Zhu, "Fourier-transform ghost imaging with hard x rays," Phys. Rev. Lett. 117, 113901 (2016)
- 41. A. Schori, D. Borodin, K. Tamasaku, and S. Shwartz, "Ghost imaging with paired x-ray photons," Phys. Rev. A 97, 063804 (2018)

Vol. 9, No. 1 / January 2022 / Optica

- T. J. Lane and D. Ratner, "What are the advantages of ghost imag-ing? Multiplexing for x-ray and electron imaging," Opt. Express 28, 5898–5918 (2020).
- 5898–5918 (2020).
 C. Li, W. Yin, H. Jiang, and Y. Zhang, "An efficient augmented Lagrangian method with applications to total variation minimization," Comput. Optim. Appl. 56, 507–530 (2013).
 A. Gatti, E. Brambilla, M. Bache, and L. A. Lugiato, "Ghost imaging with thermal light: comparing entanglement and classical correlation," Phys. Rev. Lett. 93, 093602 (2004).
- A. M. Kingston, W. K. Fullagar, G. R. Myers, D. Adams, D. Pelliccia, and D. M. Paganin, "Inherent dose-reduction potential of classical ghost imaging," Phys. Rev. A 103, 033503 (2021).
 D. Ceddia and D. M. Paganin, "Random-matrix bases, ghost imaging, and x-ray phase contrast computational ghost imaging," Phys. Rev. A 67, 062114 (2019).
- Aray phase contrast computational ghost imaging. Phys. Rev. A 97, 062119 (2018).
 X. Llovet, A. Moy, P. T. Pinard, and J. H. Fournelle, "Electron probe micro-analysis: A review of recent developments and applications in materials science and engineering," Prog. Mater. Sci. 116, 100673 (2021).

Article 3-

High-spectral resolution absorption measurements with free-electron lasers using ghost spectroscopy

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High-spectral-resolution absorption measurements with free-electron lasers using ghost spectroscopy

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We demonstrate a simple and robust high-resolution ghost spectroscopy approach for x-ray and extreme ultraviolet transient absorption spectroscopy at free-electron laser sources. To retrieve the sample response, our approach requires only an online spectrometer before the sample and a downstream bucket detector. We validate the method by measuring the absorption spectrum of silicon, silicon carbide, and silicon nitride membranes in the vicinity of the silicon $L_{2,3}$ edge and by comparing the results with standard techniques for absorption measurements. Moreover, we show that ghost spectroscopy allows the high-resolution reconstruction of the sample spectral response to optical pumps using a coarse energy scan with self-amplified spontaneous emission radiation.

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I. INTRODUCTION

X-ray and extreme ultraviolet (XUV) free-electron lasers (FELs) are very powerful and bright sources that enable measurements of ultrafast phenomena in a broad range of processes [1,2]. Short wavelength spectroscopy is widely used for the determination of the electronic structure of materials and provides element specific information on the charge and spin structures as well as bonding configurations, which are important for understanding the functionality of materials [3]. When performed at FELs, x-ray spectroscopy can provide information on the dynamics of the processes by using pump-probe schemes, where the short FEL pulse probes a process that is triggered by an external stimulus, which can be provided either by an optical laser or by the FEL itself. By varying the delay between the pump and the probe pulses, full information on the dynamics of the electronic response of the sample can be recorded [4].

There are basically two common strategies for the measurement of high-resolution absorption spectra. The first is to use narrowband (quasimonochromatic) radiation and to measure the total transmitted intensity after the sample (or the emitted fluorescence, which is often proportional to the absorption). With this approach the spectrum of the sample response is reconstructed by scanning the photon energy of the

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input radiation and registering the intensities measured by the detector for each input photon energy. The monochromaticity of the pulse is obtained either by using a monochromator [5] or by using one of the seeding schemes depending on the wavelength of the radiation [6–8]. A second strategy is implemented when the radiation has a broadband spectrum ($\Delta\lambda\lambda\lambda \sim 1\%$ or more). In this case, the spectrum of the transmitted radiation is compared with the spectrum of the input beam before the sample [9] and it is absolutely necessary to know the spectrum before and after the sample with high precision and fidelity. The energy resolution of the first approach depends on the spectral bandwidth of the input radiation whereas, in the second case, it is determined by the resolving power of the spectral measurements.

The advantages of the broad bandwidth pulse strategy are the possibility to measure broad ranges of spectra without scanning the central emission wavelength, and the availability of higher flux. Therefore, this approach can be significantly faster than the narrow bandwidth approach and useful for the measurement of low-efficiency processes. However since broad bandwidth FEL pulses are generated usually by using the process of self-amplified spontaneous emission (SASE) [10,11], the pulse energy and the spectra vary randomly from one shot to another. Thus, it is necessary to measure the spectra before and after the sample on a shot-to-shot basis. While single-shot spectrometers have been developed [12–16], the simultaneous application of two such spectrometers for these measurements is challenging, time consuming, and expensive. Furthermore, signal-to-noise (SNR) requirements impose a

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limitation on the minimum number of photons that must be detected for the reconstruction of the spectra, which leads to stringent requirements for the input flux and limits the dynamical range of absorption magnitudes that can be measured. Thus, the range of samples that can be measured with standard methods is limited. Finally, while with a narrowband pulse the absorption can be inferred from the measurement of the fluorescence yield, which is often proportional to the absorbance, in the broadband scheme it is not possible since the comparison between the two spectrometers is required. Thus, the scheme can only be applied to transmissive samples (or for samples that allow the measurement of the photocurrent), which strongly limits the choice of materials that can be studied at FELs.

From the above it is clear that the choice of experimental method depends on a range of factors: the available light source, which may be SASE only; the spectrometers available; the desired energy and temporal resolution for time-resolved experiments; and the time available for measurement, which is very often strictly limited. An alternative strategy to perform absorption spectroscopy with FEL radiation that overcomes the challenges of the above-described approaches is ghost spectroscopy (GS), which is a form of correlation spectroscopy. Being a method that relies on multiplexed measurements rather than direct measurements it presents a number of advantages, with respect to the duration of the experiment, the simplicity of the setup, and the resolution of the measurement [17]. This technique has been demonstrated with radiation in the optical range [18-21] and recently with soft x rays using SASE pulses generated by FELs [22-24]. In addition, a closely related approach has been used recently with hard x rays to measure simultaneously the unoccupied and occupied electronic states of the atom by using two spectrometers and correlation [25]. The concept of GS is also closely related to ghost imaging (GI) [26], which has been successfully applied with laboratory [27,28], synchrotron [29-33], and FEL [34] x-ray sources.

The key parameter for GS is the variation of the spectral features from one shot to another. GS indeed exploits the stochastic nature of the SASE pulse spectra, i.e., the random shot-to-shot variation of the multispike spectra. Within this method, the spectrum of radiation impinging on the sample is measured and correlated on a shot-by-shot basis with the measured intensity of a single-pixel detector (usually a photodiode) that has no spectral resolution and is mounted after the sample. The measured intensity at this detector is proportional to the integral of the product of the spectrum of the input pulse and the spectral dependence of the transmission of the sample, i.e., its transmission function. Therefore, for each pulse, if the correlation between the input spectrum and the transmission function of the sample is high, the detector measures high intensity. Conversely, if the correlation is low, it measures low intensity. By repeating this procedure for many input pulses with different spectral distributions, it is possible to reconstruct the absorption spectrum of the sample [17,35]. The term ghost here refers to the fact that neither of the detectors can provide the spectrum, in direct analogy to GI, where the pixelated detector is blind to the object and the bucket detector does not provide spatial information [26-34].

Here, we present a simple and robust approach for GS in the XUV photon-energy range that requires only one spectrometer in front of the sample and a photodiode placed behind it. By replacing the downstream spectrometer with a photodiode, our approach greatly simplifies the experimental setup for absorption measurements with SASE FELs. At most facilities only the spectrometer before the sample is permanently installed so our method eliminates the need for the precise realignment of the downstream spectrometer, which is typically required with the standard broadband approach. This saves considerable time and effort and minimizes systematic errors that can arise from imprecise alignment. Our approach thus enables more complex and precise experiments to be performed at FELs, with minimal setup and alignment requirements. By directly comparing the measurement times and the spectral resolution of the GS case with that obtained by setting the FEL emission in SASE and seeded configurations, we demonstrate that GS is an efficient strategy to perform absorption spectroscopy at FELs. Furthermore, we extend the method and demonstrate its applicability for pump-probe measurements. As with the static measurements, the transient approach provides very highenergy resolution with a significantly reduced number of measurements.

II. METHODS

A. Experimental setup and radiation properties

We conducted the experiment at the DiProI (Diffraction and Projection Imaging) end station [36,37] using the doublecascade FEL source FEL-2 of the FERMI user facility located in Trieste, Italy [38]. This source can produce either SASE FEL radiation [39] or seeded FEL pulses [7,38] depending on the setting parameters. To demonstrate our approach for GS, we tuned the SASE pulse central energy in the photonenergy range between 99 and 106 eV for the measurements of the Si $L_{2,3}$ edges. The radiation produced by the source was focused by a set of bendable Kirkpatrick-Baez mirrors [40] to a spot size of about 500 \times 600 μ m² at the sample position; the polarization was circular and the pulse duration was estimated to be about 250 fs. The repetition rate was 50 Hz. The setup of our experiment is presented in Fig. 1. The online spectrometer was the pulse-resolved energy spectrometer transparent and online (PRESTO) [16], which is mounted at FERMI after the undulators and before the end stations. In the PRESTO spectrometer, a grating delivers most of the radiation in zeroth order (97%) to the end stations, while the weaker first order of the grating is used to measure the spectrum of each pulse.

The spectrometer resolution in the working energy range is $\Delta\lambda/\lambda \sim 5 \times 10^{-5}$ [16], corresponding to an energy resolution of about 5 meV at 100 eV. Examples of the spectral distribution of the FEL pulses in the SASE configuration and the average over 8000 shots are presented in Fig. 2(a). In our experiment, we mounted the sample in the direct beam and measured three different membranes of silicon (Si), silicon nitride (Si₃N₄), and silicon carbide (SiC), 200 nm thick, provided by Norcada. The average energy per pulse at the sample plane was $18.5 \pm 3 \ \mu$ J, corresponding to a deposited energy density per pulse of $6 \pm 1 \ \text{mJ/cm}^2$, which is well below the typical damage threshold of the samples [41]. For the

HIGH-SPECTRAL-RESOLUTION ABSORPTION



FIG. 1. GS experimental scheme. The input SASE radiation is split by a grating installed at the PRESTO instrument. The first order is used as a reference that is measured by a single-shot spectrometer mounted before the sample. The zeroth order irradiates the sample and the transmitted radiation after the sample is measured by a photodiode. The pump is an optical laser that is tuned to excite the electrons form the valence band to the conduction band.

detector with no energy resolution, we used a $10 \times 10 \text{ mm}^2$ photodiode with an yttrium aluminum garnet (YAG) scintillator screen to convert the FEL radiation into optical radiation. The detector was mounted at about 500 mm downstream from the sample. At the detector position, due to the beam divergence, the FEL spot size was about $3 \times 4 \text{ mm}^2$.

For the pump-probe measurements the optical excitations were triggered by a pump laser at 3.1 eV (400 nm) with a pulse duration of about 100 fs, beam dimensions of 700 × 670 μ m², and fluence of 8.5 mJ/cm². In the experiment, we measured various delays from -5 to 150 ps and the angle between pump radiation and the sample was ~5°.

For the GS measurements and photon energies in the range of 99–106 eV we varied the central photon energy of the SASE radiation with a step size of 250 meV. At each of the SASE photon energies we measured 2000 shots and the SASE bandwidth spans a range of 500 meV [full width at half maximum (FWHM), as can be seen in Fig. 2(a)]. To account for the dependence of the beamline transmission on the photon energy, we compared the total intensities of the spectrometer and the photodiode without the sample every time we changed the central photon energy of SASE emission. For the GS measurements and photon energies in the range of 99–106 eV we varied the central photon energy of the SASE radiation with a step size of 250 meV. At each of the SASE photon energies we measured 2000 shots and the SASE bandwidth spans a range of 500 meV [FWHM, as can be seen in Fig. 2(a)].

To account for the dependence of the beamline transmission on the photon energy, we compared the total intensities of the spectrometer and the photodiode without the sample every time we changed the central photon energy of SASE emission. We eliminated the background noise of the camera of the spectrometer by subtracting the dark reference images collected without FEL illumination.

Since GS is based on the intensity correlation between the spectral features recorded on the spectrometer and the intensity fluctuation recorded by the single-pixel detector placed behind the sample, it was important to ensure a highly linear correlation between the total recorded intensities on the two detectors in the absence of the sample. To compare the correlation quality between the two devices, we define the relative error "R" for each *i*th pulse as

$$R_i = \frac{I_{S_i}/\langle I_S \rangle - I_{P_i}/\langle I_P \rangle}{I_{P_i}/\langle I_P \rangle},\tag{1}$$

where I_{S_i} and I_{P_i} are the total intensity of the *i*th shot, measured by the spectrometer and the photodiode, respectively, and $\langle \cdots \rangle$ represents an average over all pulses.

We found that the typical standard deviation of the relative error distribution of our experimental setup was about 7.5%. A typical distribution of the relative intensity errors between the two detectors, for an ensemble of 36 000 FEL pulses at a variety of energies within our scan range, is presented in Fig. 2(b). The main contributions to the error distribution are (1) The contamination of the high harmonics generated by the source that is not suppressed by the optics before the spectrometer; (2) the shot-to-shot beam pointing jitter, which is important



FIG. 2. (a) Energy distribution of the SASE pulses measured by the online spectrometer, when the central photon energy is set at 100.5 eV. The thinner lines are the spectra of four individual pulses and the thick green line is the average over 8000 pulses. (b) The relative error distribution between the total intensities at the spectrometer and the photodiode averaged over 36000 pulses (blue bins). The red line is the Gaussian fit and the standard deviation is 7.5%.

since the spectrometer and the bucket detector detect slightly different portions of the beam; (3) the presence of off-axis spurious radiations that can impose spatial dependence of the spectral components; (4) the impact of the finite dimensions of the beamline mirrors, which may clip the beam; (5) shot noise. However, as we show in the next section, the error distribution we observed is sufficiently small for the GS reconstruction.

B. Seeded radiation and synchrotron measurements

To compare the method of GS with conventional scanning approaches, we used FERMI FEL radiation in the seeded configuration, where the FEL pulses are generated using a -100 fs (FWHM) external laser pulse in the ultraviolet range from 4.7 to 4.9 eV to trigger the FEL amplification process [7,38]. By using a harmonic upshift factor of 21 the output radiation spans a photon energy from 99 to 103 eV. As shown in [42] the seeded FEL generated at FERMI is close to the Fourier limit and the pulse duration is estimated to be about 30 fs [43]. In this experiment the normalized FWHM bandwidth is $\Delta\lambda/\lambda = 1 \times 10^{-3}$, equivalent to an energy resolution of about 100 meV at 100 eV. Therefore, we scanned the photon energy of the seeded radiation with step sizes of 75 meV and measured the transmission of the silicon membrane near the $L_{2,3}$ edges in a range comparable to the GS measurement. The transmission of the membrane at each photon energy was calculated as the ratio between the average pulse energy detected by the photodiode and the average total pulse energy detected by the spectrometer. In addition, we performed the same procedure for the SASE scanning: in this case, almost all the electron bunch participates in the FEL process, resulting in a FEL pulse duration of about 250 fs (FWHM)

To validate our method, we compared the spectra we measured at FERMI with spectral measurements of the same samples at the BEAR beamline at the Elettra synchrotron [44]. In this latter case, the spectral sample transmission at each energy point is simply the average intensity measured after the sample divided by the input average intensity.

C. GS reconstruction procedure

To reconstruct the ghost spectrum for each SASE central energy, we exploited the following reconstruction procedure. We represent the intensities of the *N* pulses measured by the photodiode by a vector \mathbf{T} (test data). The spectra of the pulses are represented by the matrix \mathbf{A} for which every row is the spectral distribution of a single pulse (reference data). We represent the transmission function of the sample as a vector \mathbf{x} , and thus the vector \mathbf{T} is equal to the product of the matrix \mathbf{A} and the vector \mathbf{x} :

$$\mathbf{A}\mathbf{x} = \mathbf{T}.$$
 (2)

In GS experiments, we measure the vector **T** and the matrix **A**. We are interested in solving Eq. (2) for the vector **x** using the compressive sensing (CS) algorithm of "total variation minimization by augmented Lagrangian and alternating direction algorithms" (TVAL3) [45]. However, this algorithm works well only when the width of the average spectrum is much broader than the spectral range under investigation.

Unfortunately, the SASE bandwidth in our case was narrower than the total measured spectral range. To overcome this challenge, we used the following procedure: first we normalized the matrix of the raw data by the average SASE distributions [for example, for the central photon energy at 100.5 eV we used the green line in Fig. 2(a)]:

$$\mathbf{B}_{i,j} = \frac{\mathbf{A}_{i,j}}{\frac{1}{N} \sum_{k=1}^{N} \mathbf{A}_{k,j}}.$$
(3)

Next, we normalized the reference and the test data by the pulse energy of each pulse:

F

$$\mathbf{C}_{i,j} = \frac{\mathbf{B}_{i,j}}{\frac{1}{M} \sum_{k=1}^{M} \mathbf{B}_{i,k}}, \quad \mathbf{T}'_i = \frac{\mathbf{T}_i}{\frac{1}{M} \sum_{k=1}^{M} \mathbf{B}_{i,k}}.$$
 (4)

By using this procedure, we can replace Eq. (2) with a new equation,

$$\mathbf{C}\mathbf{x}' = \mathbf{T}',\tag{5}$$

where the matrix representing the different energy distributions in each pulse is now the effective matrix \mathbf{C} where the envelope is normalized and the shot-to-shot intensity variations are filtered out.

Next, we used the TVAL3 algorithm to solve Eq. (5). The basic idea of TVAL3 is to recognize that the gradients of the measured spectra can be represented by a sparse vector. The vector \mathbf{x}' is reconstructed by minimizing the augmented Lagrangian,

$$\min_{\mathbf{x}'} \sum_{j=1}^{M} \|D_j \mathbf{x}'\|_2 + \frac{\mu}{2} \|\mathbf{C} \mathbf{x}' - \mathbf{T}'\|_2^2 \text{ subject to } \mathbf{x}' \ge 0, \quad (6)$$

with respect to the l_2 norm. In Eq. (6), $D_j \mathbf{x}'$ is the *j*th component of the discrete gradient of the vector \mathbf{x}' , and μ is the penalty parameter of the model (here we set $\mu = 2^6$). We note that for the reconstruction of the transmission function of the sample (the vector \mathbf{x}') the vector \mathbf{x}' that we obtained by using the described algorithm is renormalized to obtain

$$\mathbf{x}_j = \frac{\mathbf{x}'_j}{\frac{1}{N} \sum_{k=1}^N \mathbf{A}_{k,j}}.$$
(7)

The mathematical justification for this procedure is described in the Appendix.

After we reconstructed separately the absorption spectrum for each SASE central energy of the SASE scan, we merged all the absorption spectra to create the spectrum of the sample. At this point, the number of data points is much larger than the number of points corresponding to the GS resolution since, as we will discuss below, the resolution of GS is determined by the width of the individual spectral spikes [46], which are broader than the resolution of the spectrometer. Therefore, the final step was to bin the points to obtain a bin size equal to the spike width.

III. RESULTS AND DISCUSSION

A. Ghost spectroscopy results

The GS results for the three samples are presented in Fig. 3. The blue dots are the GS reconstructions, and the magenta



FIG. 3. GS $L_{2,3}$ edge spectra of (a) silicon carbide (SiC), (b) silicon nitride (Si₃N₄), and (c) silicon (Si). The blue dots are the GS results, and the magenta (light gray) dots are the results obtained by the monochromatic synchrotron measurements.

(light gray) dots are the results of the synchrotron monochromatic scan that we used to validate our method. It is clear from Fig. 3 that the agreement between the GS reconstruction using the FEL and the synchrotron measurements is very good. We conclude that the energetic chemical shift of the Si $L_{2,3}$ resonances in the three different samples due to the different Si bonding is well monitored by GS reconstruction. Furthermore, the contribution of the spin orbit splitting to the $L_{2,3}$ edge is clearly visible in the absorption spectrum of crystalline Si near 100.2 eV of the silicon membrane [47] and indicates that the GS resolution is much better than the width of each of the edges, which is around 100 meV. The agreement with the spectra measured by the synchrotron also indicates that the resolution of the GS is close to the resolution of the synchrotron, which is about 30 meV.

To compare the GS method, the scanning of the seeded radiation method, and the scanning of the SASE radiation method, we plot the spectra measured by these three different approaches for the Si sample in Fig. 4(a).

While the photon-energy resolutions of the seeded and the SASE radiation are simply determined by the spectral width of their pulse envelopes, the resolution of GS is mostly related to the spectral width of each individual spike of the SASE spectrum. More precisely, we estimated the resolution of the three methods by calculating the FWHM of the autocorrelation function and by dividing it by $\sqrt{2}$. This protocol provides the spectral width of the individual spikes for GS [46] and the spectral width for the SASE and the seeded radiations. The autocorrelation function values of the SASE pulses averaged over 2000 pulses are the black dots in Fig. 4(b). The magenta line is a fit of the sum of two Gaussian curves. The two curves represent the spectral width of the SASE pulse and the width of the spectral spikes. Using the same procedure, we present the autocorrelation function of the seeded pulses in Fig. 4(c), where the narrower Gaussian corresponds to the spectral width of the seeded pulse. In Fig. 4(d) we present these three Gaussian fits that correspond to the energy resolutions of the SASE (green dashed line), seeded (red dotted line), and GS (blue solid line), respectively. It is important to note that the spectral width of the SASE radiation determines



FIG. 4. (a) Comparison of the GS results (blue dots) with the spectrum collected by scanning FEL pulses generated in the seeded (red squares) and the SASE (green circle) configurations. The statistical error of the SASE and seeded measurements was about 1% and too small to be seen. (b), (c) Averaged autocorrelation function of SASE and seeded radiation, respectively. The black dots are the values of the autocorrelation function that are calculated from the measured data and the magenta line is a fit of the sum of two Gaussians. The orange dashed line is an example of a single-shot spectrum. (d) Gaussian fits from the autocorrelation function, which we used for the calculation of the resolutions of the three methods. The resolutions are 500, 75, and 35 meV for SASE, seeded, and GS methods, respectively.

the spectral range of the GS reconstruction at each of the SASE central photon-energy steps.

The widths of the Gaussian profiles reported in Fig. 4(d) indicate clearly that GS provides a higher resolution than the one reached in seeded mode and much higher than the SASE case, but with a number of scans that is equal to the number of scanning points used in SASE mode. For the same spectral range from 99 to 103 eV, with GS we used 15 steps and the resolution was 35 meV; with the SASE radiation we also used 15 steps, but the resolution was only 500 meV; and with the seeded radiation we used 51 steps and the resolution was 75 meV.

In principle, it is possible to increase the spectral resolution in seeded mode by increasing the duration of the optical laser seeding pulse, but at the expense of increasing the number of step points per scan to map a given spectral interval. For GS the trade-off between the resolution and the number of step points is lifted.

B. Number of pulses required for the reconstruction of the spectrum

In the previous section, we showed that GS requires a smaller number of step points per scan compared with the seeded radiation to cover the same spectral range. However, the measurement time also depends on the number of shots required to stabilize the result at each energy point, which is different between the GS and the seeded beam scans.

A seeded FEL behaves indeed as a laserlike source [48] and has stable output wavelength and power. An ideal measurement of the input wavelength and of the pulse energy before and after the sample would be sufficient to measure one sample of the absorption spectrum with a single FEL shot. In practice, the noise associated to the energy detection as well as the loss due to photon transport reduces the correlation between the two energy measurements, and even the acquisition of a single spectral sample requires averaging over a number of shots to improve the signal-to-noise ratio.

Conversely, in GS the spectrum reconstruction requires a set of spectral acquisitions. The single measurement provides only a fraction of the spectral information at each frequency sample, but simultaneously on the samples distributed over the broad range of frequencies corresponding to the SASE pulse bandwidth. The SASE spectrum has the structure of spikes of random amplitude and distribution; the fluctuation statistics of each bin in the measured spectrum depends therefore on the width of the bin itself. The highest achievable spectral resolution with GS corresponds to spectral bins separated by a width comparable to the spike spectral width. Increasing the bin size reduces the spectral resolution, but improves the statistics collected at each shot and requires a lower number of shots to ensure the convergence of the analysis. It has been shown for GI that the number of iterations scales as the number of the pixels in the reconstructed image [49] and we expect a similar dependence for GS. To test this important aspect, we first compared the dependence of the quality of the absorption spectrum measurements on the number of shots for the GS and the seeded radiation.

To quantify the quality of the reconstructed spectrum we consider the synchrotron data as the accurate reference absorption spectrum and define the mean absolute error $\langle \varepsilon \rangle$ as

$$\langle \varepsilon \rangle = \frac{1}{M} \sum_{i=1}^{M} |x_i - g_j|, \qquad (8)$$

where x_j is the *j*th point in the reconstructed spectrum (by GS or seeded), g_j is the *j*th point in the ground truth which is the synchrotron measurement, and *M* is the number of points.

We plot $\langle \varepsilon \rangle$ as a function of the number of shots for the GS (blue dots) and for the seeded radiation (red squares) in Fig. 5(a). The comparisons (in addition to the synchrotron measurement as a reference) for various numbers of shots per scanning point are shown in Figs. 5(c)–5(h). In our experiment the spectrum we reconstructed by GS was slightly closer to the synchrotron results than the spectrum obtained with the seeded radiation. The smallest $\langle \varepsilon \rangle$ for GS is around 0.035 and for the seeded radiation it is 0.055. This comparison indicates that GS can provide high-quality spectra with a number of pulses per point that is comparable to the seeded radiation

The small difference between the GS results and the seeded radiation results may indicate a systematic error and thus it is difficult to infer from Fig. 5(a) which method converges to its best value faster. We therefore defined the "convergence factor," C_F , similarly to the above definition of the $\langle \varepsilon \rangle$ as

$$C_F = \frac{1}{M} \sum_{j=1}^{M} |x_j - b_j|,$$
(9)

where now b_i represents the best value for GS and for the seeded mode separately, which is the *j*th point in the reconstructed spectrum using 2000 pulses for GS and seeded radiation. For this comparison we bin the GS dataset to 35 meV, corresponding to the value used in the plots 5(a) and 5(c)-5(f) (blue-solid line) and 75 meV to match the resolution of the seeded radiation (blue dashed line). In Fig. 5(b) we show the C_F for the GS and for the seeded radiation scans as a function of the number of pulses per scanning point in the three cases. The convergence of GS is comparable to the convergence of the seeded mode at equal resolution and slower when the resolution of the GS is higher, requiring more shots to reach a similar C_F . This implies that when the resolution is equal the required number of shots per data point with the GS and with the seeded radiation are comparable; hence the measurement time with GS is shorter than with the seeded radiation.

Another interesting result from this comparison is that even with a small number of 300 pulses per scanning point, the quality of the reconstructed spectrum obtained by GS was sufficient to resolve the main features of the Si $L_{2,3}$ edge spectrum. In our experiment the repetition rate was 50 Hz and the number of scanning points for the GS was 15, which implies that the measurement time was 90 s.

C. Compression factor dependence

As discussed in the previous sections the resolution of GS is determined by the average width of the single SASE

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FIG. 5. (a) The mean absolute error and (b) convergence factor of the reconstructed spectrum of the silicon membrane as a function of the number of pulses per scanning point for the GS (blue dots) and the seeded radiation (red squares). (c)–(h) The reconstructed spectrum results with GS (blue circles) and with seeded radiation (red squares) compared to the synchrotron measurements (magenta line) as a guide using (c) 10, (d) 50, (e) 100, (f) 300, (g) 1000, and (h) 2000 pulses per scanning point.

spectral spikes. The main parameter that we can use to control the spike width is the electron bunch compression factor [50]. To compress the electron bunch, we used a magnetic double chicane located inside the acceleration section of the FERMI source. A typical compression is used at FERMI to increase the peak current up to about 650 A [51]. The compressor can be tuned to further compress the beam to reach a higher peak current. In Fig. 6(a) we show typical energy pulse spectra for a modestly compressed electron beam (blue line) and for a highly compressed electron bunch (purple dots), respectively. The two graphs clearly show that the primary spectral features are different in the two regimes, with more and wider spikes for a highly compressed electron beam. To demonstrate this dependence more quantitatively we show in Fig. 6(b) the spike width (calculated by the FWHM of the autocorrelation Gaussians divided by $\sqrt{2}$) as a function of the peak current. The results indicate that the spectral spike's width grows linearly with the compression of the electron beam, which is in agreement with the previous study [50]. In our experiment the peak current was about 900 A, corresponding to a spectral width of 35 meV, while for higher current (i.e., 2150 A) the width is about 60 meV. The conclusion from this discussion is that by controlling the compression factor it is possible to control the spectral resolution of our approach. It is important to note, however, that the compression also affects the coherence and the pulse duration of the SASE emission [50,52].



FIG. 6. (a) Typical single-shot FEL pulse spectra for 845 A (blue solid line) and 2080 A (purple dotted line) of the peak current of the electron bunch. (b) Spike width as a function of the peak current. The vertical error bars represent the uncertainty caused by the spectrometer resolution and the fitting procedure.



FIG. 7. Photoinduced absorption variation in the silicon membrane: (a) XUV absorption spectra at various pump delays. (b) Differential absorption map.

D. Pump-probe measurements

To demonstrate the ability to measure photoinduced variation in the *L*-edge absorption spectrum with GS we plot the spectra at -5 ps (before the arrival of the optical pulse), 1, 25, and 150 ps delays between the optical pump and the XUV pulses in Fig. 7(a).

The largest differences between the photoexcited and the ground state spectrum can be clearly seen at a delay of 1 and 25 ps for photon energies that are slightly above the L_3 edge (from 99.8 to 100.3 eV) and below the edges.

For a better understanding of the dynamics of the photoinduced effects we numerically calculated the differential absorbance by subtracting absorbance at -5 ps, where the probe arrives before the pump, from the absorbance at a particular delay and plotted the results in Fig. 7(b). The color maps were produced by interpolation with the measured data from -5 to 150 ps. Inspecting Fig. 7(b), we see several different behaviors in the dynamics of the variation of the spectrum. To interpret Fig. 7(b), we recall that the L_3 and the L_2 edges are at about 99.8 and 100.3 eV, respectively, and that they correspond to excitations from the 2p states (the upper- and lower-spin states, respectively) to the bottom of the conduction band. We first explain the results of Fig. 7(b)by considering the dynamics of the charge carriers. Since the photon energy of the optical laser is 3.1 eV, it excites electrons from the valence band to the direct valley (the Γ point) of the conduction band. Thus, immediately after the excitation of the electrons, the number of unoccupied states at the Γ point is reduced, and holes are created in the valence band. At delays longer than the optical pulse duration, the charge carriers relax from their excited state, first by electron-electron scattering and at later times (several ps) by electron-phonon scattering [53]. As a result of the relaxation processes, the electrons lose energy and temporarily occupy states at energies lower than the Γ point in the conduction band and inside the gap (i.e., isolated impurity states); they eventually relax back to the valence band by Auger recombination after several tens of ps [53]. Thus, we expect the charge carrier dynamics to lead to a reduction in the absorption near 99.8 eV and to an increase in the absorption below 98.7 eV. Since the transition from the 2p level to the Γ point is dipole forbidden [53] and since the temporal resolution in our experiment was \sim 350 fs, we observed only the slower relaxation dynamics. The relaxation from the Γ point to the bottom of the conduction band and to the gap states is clearly seen in the form of the reduction in the absorption in the energy range from 98.8 to 99.8 eV and from 99.9 to 101.7 eV from a delay of 0 ps to a delay of 25 ps and again from a delay of 25–150 ps.

However, there are several interesting features in Fig. 7(b) that cannot be explained by considering only excitations and relaxations of charge carriers. These are the increased absorption in the narrow area between 99.8 and 99.9 eV and the trend of the variation at delays between 1 and 7 ps. The discrepancy between the observations and the explanation based on charge carrier dynamics indicates a possible photoinduced modification of the band structure of the silicon and related structural changes.

If these photoinduced variations exist, they should lead to shifts of the edges and to further variations of the absorbance of the sample mainly near the edges. We therefore plot the delay dependence of positions of the edges in Figs. 8(b)-8(d).

We estimate the edge position by numerically calculating the derivative of the absorbance spectrum. This derivative peaks at the edges as can be seen in the examples for 0 and 25 ps delays shown in Fig. 8(a). This figure clearly shows that the L_3 edge shifts from 99.79 \pm 0.035 to 99.87 \pm 0.035 eV after 25 ps from the optical stimulus. The same behavior is observed at the L_2 edge lying at 100.30 \pm 0.035 and 100.40 \pm 0.035 eV, at 0 and 25 ps delay, respectively. The other two peaks observed in Fig. 8(a) below the *L* edges can be attributed to impurity states in the Si gap.

The full dynamics of the $L_{2,3}$ edges are reported in Figs. 8(b) and 8(c). We can see that the L_3 and the L_2 states shift to lower photon energies from 3 to 5 ps. From 5 to 7 ps both edges returned to their original positions. Again from 7 to 25 ps both the edges exhibit negative shifts and then they return to their original position after 150 ps. The largest shift of the L_3 edge is -0.08 eV and the largest shift of the L_2 edge is -0.10 eV, occurring at 25 ps delay. While obviously we did not measure sufficient delays in the region near the largest deviation, the results are consistent with the theory that predicts that a few ps after the excitations the conduction band is shifted toward the valence band [54] and with pertinent publications [55]. This can explain the positive variation of the absorption just below the edge, which we see in Fig. 7(b) since the shift of the conduction band and the



FIG. 8. Variation of the edge position: (a) derivatives of the absorption spectra of at 0 and 25 ps delays. (b) The change of the position of the L_3 edge with the delays. (c), (d) Enlarged view of the change of the position of the L_2 and L_3 edges, respectively, from –5 to 25 ps.

corresponding change in the density of states near the bottom of the band can lead to this positive variation. The shift at a delay of several ps can be attributed to electron-phonon interaction and the shift at longer delays to the change in the structure of the silicon that leads to the variation in the band gap. The nonmonotonic behavior has to be investigated in detail and suggests that several processes can impact the variation of the band gap, for example, the temperature and pressure of the hot charge carriers. Since the spectral resolution in our experiment was 35 meV, the small positive shifts we see in Fig. 8 are smaller than our experimental precision.

Comparing our results with pertinent work on transient XUV spectroscopy in silicon, we note that Leone and colleagues [53] reported a detailed study of the transient photoinduced variation of the absorption spectrum by using a high harmonic generation source as the probe and with optical pumps at several wavelengths. The time resolution in their experiment was higher than ours; thus they could monitor the dynamics on the 100 fs scale. The intensity of the optical laser they used was about an order of magnitude weaker than the intensity we used, and their spectral resolution (500 meV) was lower than ours. Most of our results agree with that work and with the theoretical models they suggested. The main differences are due to the higher intensity in the present work, which led to more pronounced variations in the band structure. Since we had a better spectral resolution, we observed several structures they did not observe (the edge shifts, in particular), but they all agree with the theory.

In another work, Beye *et al.* [55] reported a photoinduced phase transition with the optical fluence of 250 mJ/cm^2 , which is about just 30 times higher than the fluence used here. In their experiment they also used a 400 nm laser, but they measured the XUV fluorescence. The shift of 80 meV

for L_3 and 200 meV for L_2 which we observed when the optical fluence was 8.5 mJ/cm² suggests that a photoinduced phase transition can occur only if the fluence dependence of the variation in the band structure is highly nonlinear. This is because the band gap is about 1.1 eV.

IV. CONCLUSION

In this paper we have demonstrated the implementation of GS for an XUV FEL with an online spectrometer in front of the sample and a photodiode after the sample. The experimental setup is simple and can provide high spectral resolution with SASE FELs without additional spectrometers after the sample or monochromatizating the input beam. We have validated the quality of the absorption spectrum measurements by comparing to more conventional methods and found that the spectral resolution is comparable to the resolution of scans with seeded radiation. Our results indicate that the measurement time with GS can be significantly shorter than the measurement time with seeded radiation. From our analysis we conclude that the reduction in the measurement time is comparable to the ratio of the average spectral width of the SASE regime to the spectral width of the seeded one at a comparable spectral resolution. We emphasize that we do not expect that GS will be always faster than scans with quasimonochromatic radiation and stress that the exact conditions depend on various details such as the specific properties of the FEL and the sparsity of the absorption spectrum. The spectral resolution of the GS method is determined by the lower resolution of either the width of spectral autocorrelation of the SASE radiation or the resolution of the spectrometer. Our work therefore calls for the improvement of the resolution of single-shot spectrometers and for the reduction of the spectral width of the SASE spikes.

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The results of the pump-probe experiment that we present demonstrate the applicability of ghost spectroscopy for transient absorption spectroscopy and for the study of photoinduced effects with high-photon-energy FELs. The method can lead to a novel and efficient procedure for transient spectroscopy at high photon energies. It is important to note that the time resolution in our method is limited by the pulse duration of the input pump and probe pulses, while the spectral resolution is limited by the width of the spectral spikes. This trade-off between the time and the spectral resolution, that find their optimum for Fourier transform limited pulses, has to be considered when designing measurements with ghost spectroscopy.

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APPENDIX: RECONSTRUCTION PROCEDURE FOR GHOST SPECTROSCOPY WHEN USING SASE FLUCTUATIONS

In the following paragraphs we provide further details on the derivation of the equations we used for the reconstruction of the absorption spectrum from the measured data in the experiment of ghost spectroscopy (GS).

To reconstruct the absorption spectrum of the object is we need to solve Eq. (2) of the main text:

$$\mathbf{T} = \mathbf{A}\mathbf{x},\tag{A1}$$

where **T** is a vector that includes the intensities of *N* pulses measured by the photodiode, **x** is a *P*-length vector representing the transmission function of the sample, and **A** is a $N \times M$ matrix where every row represents the spectral distribution of a single pulse. However, the raw data from the measurements include not just the spectral response of the sample but also the constant envelope of the SASE fluctuations [the green line shown in Fig. 2(a) of the main text] and the shot-to-shot intensity instability, which is a general property of FELs. It is therefore necessary to eliminate the information that is not directly related to the sample. The idea of the procedure below is to exploit an auxiliary matrix **C** that contains the spectral information without the SASE envelope and to normalize the shot-to-shot intensity variation.

We recall that we can represent each element of the matrix **A** as

$$\mathbf{A}_{i,j} = a_i \mathbf{A}_{i,j}^* \mathbf{F}_j,\tag{A2}$$

where the spectral envelope is the *M*-length vector **F** and the shot-to-shot intensity variation is represented by a_i for each *i*th shot. $A_{i,j}^*$ is a random value from a normal distribution, i.e., $A_{i,j}^* \sim N(\mu, \sigma^2)$. By inserting Eq. (A2) into Eq. (A1) we get

$$\mathbf{T}_{i} = \sum_{j=1}^{M} \mathbf{A}_{i,j} \mathbf{x}_{j} = \sum_{j=1}^{M} a_{i} \mathbf{A}_{i,j}^{*} \mathbf{F}_{j} \mathbf{x}_{j} = \frac{a_{i}}{a} \sum_{j=1}^{M} \mathbf{A}_{i,j}^{*} a F_{j} \mathbf{x}_{j}$$
(A3)

where *a* is defined as $a = \frac{1}{N} \sum_{i=1}^{N} a_i$. To use the matrix for the reconstruction of the absorption spectrum we define the new matrix and vectors as

$$\mathbf{x}'_{j} = a\mathbf{F}_{j}\mathbf{x}_{j}, \quad \mathbf{B}_{i,j} = \frac{a_{i}}{a}\mathbf{A}^{*}_{i,j} = \frac{\mathbf{A}_{i,j}}{a\mathbf{F}_{j}}, \tag{A4}$$

and Eq. (A3) can be transformed to

which is equivalent to $\mathbf{T} = \mathbf{B}\mathbf{x}'$.

The matrix \mathbf{B} contains the data of the spectral distribution of the input pulses normalized by the average spectral envelope of the raw measurements.

 $\mathbf{T}_{i} = \sum_{j=1}^{r} \mathbf{A}'_{i,j} \mathbf{x}$

Assuming $A_{i,j}^* \sim N(1, \sigma^2)$ and $a_i \sim N(a, \sigma^2)$, the envelope *a*F can be calculated by averaging over all the raw pulses:

$$\frac{1}{N}\sum_{i=1}^{N} A_{i,j} = \frac{1}{N}\sum_{i=1}^{N} a_i A_{i,j}^* F_j = aF_j$$
(A6)

Thus, the matrix **B** is related to the matrix **A** by

$$\mathbf{B}_{i,j} = \frac{\mathbf{A}_{i,j}}{a\mathbf{F}_j} = \frac{\mathbf{A}_{i,j}}{\frac{1}{N}\sum_{k=1}^N \mathbf{A}_{k,j}},\tag{A7}$$

which is Eq. (3) of the main text.

1

To address the second challenge of the shot-to-shot intensity variation we normalized each measurement \mathbf{T}_i by the value a_i (and for convenience we multiply also by a constant factor $\frac{a}{M}$):

$$T'_{i} = \frac{a}{P} \frac{T_{i}}{a_{i}}.$$
 (A8)

Using Eq. (A5) we can write

T

C

$$a_{i}^{\prime} = \frac{a}{M} \frac{1}{a_{i}} \sum_{j=1}^{M} B_{i,j}$$
 (A9)

and

$$a_{i,j} = \frac{a}{M} \frac{B_{i,j}}{a_i}.$$
 (A10)

This leads to

$$\boldsymbol{T}_{i}^{\prime} = \sum_{i=1}^{M} \mathbf{C}_{i,j} \mathbf{x}_{j}^{\prime} \quad \text{or} \quad \mathbf{T}^{\prime} = \mathbf{C} \mathbf{x}^{\prime}. \tag{A11}$$

which is Eq. (5) of the main text. The matrix **C** contains spectral data that we used for the reconstruction of the transmission function of the object. They are separated from the envelope of the measured spectra and normalized to have equal pulse energy. The factor a_i is calculated by

$$\frac{a}{M} \sum_{j=1}^{M} B_{i,j} = \frac{1}{P} \sum_{j=1}^{M} \frac{A_{i,j}}{F_j} = \frac{1}{M} \sum_{j=1}^{M} \frac{a_i A_{i,j}^* F_j}{F_j}$$
$$= \frac{1}{M} \sum_{j=1}^{M} a_i A_{i,j}^* = a_i \frac{1}{M} \sum_{j=1}^{M} A_{i,j}^* = a_i.$$
(A12)

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The vector T^\prime and the matrix C are related to the vector T and the matrix B by the relations

$$\mathbf{T}_{i}^{'} = \frac{a}{M} \frac{T_{i}}{a_{i}} = \frac{a}{M} \frac{\mathbf{T}_{i}}{\frac{a}{M} \sum_{k=1}^{M} \mathbf{B}_{i,k}} = \frac{\mathbf{T}_{i}}{\sum_{k=1}^{M} \mathbf{B}_{i,k}} \quad \text{and}$$
$$\mathbf{C}_{i,j} = \frac{a}{M} \frac{B_{i,j}}{a_{i}} = \frac{\mathbf{B}_{i,j}}{\sum_{k=1}^{M} \mathbf{B}_{i,k}}, \quad (A13)$$

- N. Huang, H. Deng, B. Liu, D. Wang, and Z. Zhao, Features and futures of x-ray free-electron lasers, Innovation 2, 100097 (2021).
- [2] C. Pellegrini, The development of XFELs, Nat. Rev. Phys. 2, 330 (2020).
- [3] P. Sedigh Rahimabadi, M. Khodaei, and K. R. Koswattage, Review on applications of synchrotron-based x-ray techniques in materials characterization, X-Ray Spectrom. 49, 348 (2020).
- [4] M. Maiuri, M. Garavelli, and G. Cerullo, Ultrafast spectroscopy: State of the art and open challenges, J. Am. Chem. Soc. 142, 3 (2020).
- [5] Y. Obara, H. Ito, T. Ito, N. Kurahashi, S. Thürmer, H. Tanaka, T. Katayama, T. Togashi, S. Owada, Y.-i. Yamamoto, S. Karashima, J. Nishitani, M. Yabashi, T. Suzuki, and K. Misawa, Femtosecond time-resolved x-ray absorption spectroscopy of anatase TiO₂ nanoparticles using XFEL, Struct. Dyn. 4, 044033 (2017).
- [6] S. Ackermann, A. Azima, S. Bajt, J. Bödewadt, F. Curbis, H. Dachraoui, H. Delsim-Hashemi, M. Drescher, S. Düsterer, B. Faatz *et al.*, Generation of Coherent 19- and 38-nm Radiation at a Free-Electron Laser Directly Seeded at 38 nm, Phys. Rev. Lett. **111**, 114801 (2013).
- [7] E. Allaria, R. Appio, L. Badano, W. A. Barletta, S. Bassanese, S. G. Biedron, A. Borga, E. Busetto, D. Castronovo, P. Cinquegrana *et al.*, Highly coherent and stable pulses from the FERMI seeded free-electron laser in the extreme ultraviolet, Nat. Photonics 6, 699 (2012).
- [8] D. Xiang, E. Colby, M. Dunning, S. Gilevich, C. Hast, K. Jobe, D. McCormick, J. Nelson, T. O. Raubenheimer, K. Soong *et al.*, Demonstration of the Echo-Enabled Harmonic Generation Technique for Short-Wavelength Seeded Free Electron Lasers, Phys. Rev. Lett. **105**, 114801 (2010).
- [9] G. Brenner, S. Dziarzhytski, P. S. Miedema, B. Rösner, C. David, and M. Beye, Normalized single-shot x-ray absorption spectroscopy at a free-electron laser, Opt. Lett. 44, 2157 (2019).
- [10] E. L. Saldin, E. V. Schneidmiller, and M. V. Yurkov, *The Physics of Free Electron Lasers* (Springer Science & Business Media, Berlin, 1999).
- [11] S. V. Milton, E. Gluskin, N. D. Arnold, C. Benson, W. Berg, S. G. Biedron, M. Borland, Y.-C. Chae, R. J. Dejus, P. K. Denhartog *et al.*, Exponential gain and saturation of a selfamplified spontaneous emission free-electron laser, Science 292, 2037 (2001).
- [12] N. Kujala, W. Freund, J. Liu, A. Koch, T. Falk, M. Planas, F. Dietrich, J. Laksman, T. Maltezopoulos, J. Risch *et al.*, Hard x-ray single-shot spectrometer at the European x-ray free-electron laser, Rev. Sci. Instrum. **91**, 103101 (2020).

which lead to Eq. (4) of the main text. By using the definition of \mathbf{x}' from Eq. (A4) we can find the actual transmission by using the relation

$$\mathbf{x}_j = \frac{\mathbf{x}'_j}{\mathbf{a}\mathbf{F}_j} = \frac{\mathbf{x}'_j}{\frac{1}{N}\sum_{k=1}^N \mathbf{A}_{k,j}},\tag{A14}$$

which leads to Eq. (7) of the main text.

- [13] J. Rehanek, M. Makita, P. Wiegand, P. Heimgartner, C. Pradervand, G. Seniutinas, U. Flechsig, V. Thominet, C. W. Schneider, A. R. Fernandez *et al.*, The hard x-ray photon single-shot spectrometer of SwissFEL—initial characterization, J. Instrum. **12**, P05024 (2017).
- [14] Y. Inubushi, I. Inoue, J. Kim, A. Nishihara, S. Matsuyama, H. Yumoto, T. Koyama, K. Tono, H. Ohashi, K. Yamauchi *et al.*, Measurement of the x-ray spectrum of a free electron laser with a wide-range high-resolution single-shot spectrometer, Appl. Sci. 7, 584 (2017).
- [15] J. Rehanek, C. J. Milne, J. Szlachetko, J. Czapla-Masztafiak, J. Schneider, T. Huthwelker, C. N. Borca, R. Wetter, L. Patthey, and P. Juranic, A compact and versatile tender x-ray singleshot spectrometer for online XFEL diagnostics, J. Synchrotron Radiat. 25, 16 (2018).
- [16] C. Svetina, D. Cocco, N. Mahne, L. Raimondi, E. Ferrari, and M. Zangrando, PRESTO, the on-line photon energy spectrometer at FERMI: Design, features and commissioning results, J. Synchrotron Radiat. 23, 35 (2016).
- [17] T. J. Lane and D. Ratner, What are the advantages of ghost imaging? Multiplexing for x-ray and electron imaging, Opt. Express 28, 5898 (2020).
- [18] P. Janassek, S. Blumenstein, and W. Elsäßer, Ghost Spectroscopy with Classical Thermal Light Emitted by a Superluminescent Diode, Phys. Rev. Appl. 9, 021001 (2018).
- [19] P. Janassek, A. Herdt, S. Blumenstein, and W. Elsäßer, Ghost spectroscopy with classical correlated amplified spontaneous emission photons emitted by an erbium-doped fiber amplifier, Appl. Sci. 8, 1896 (2018).
- [20] C. Amiot, P. Ryczkowski, A. T. Friberg, J. M. Dudley, and G. Genty, Supercontinuum spectral-domain ghost imaging, Opt. Lett. 43, 5025 (2018).
- [21] S. Rabi, S. Meir, R. Dror, H. Duadi, F. Baldini, F. Chiavaioli, and M. Fridman, Spectral ghost imaging for ultrafast spectroscopy, IEEE Photonics J. 14, 1 (2022).
- [22] T. Driver, S. Li, E. G. Champenois, J. Duris, D. Ratner, T. J. Lane, P. Rosenberger, A. Al-Haddad, V. Averbukh, T. Barnard et al., Attosecond transient absorption spooktroscopy: A ghost imaging approach to ultrafast absorption spectroscopy, Phys. Chem. Chem. Phys. 22, 2704 (2020).
- [23] S. Li, T. Driver, O. Alexander, B. Cooper, D. Garratt, A. Marinelli, J. P. Cryan, and J. P. Marangos, Time-resolved pump-probe spectroscopy with spectral domain ghost imaging, Faraday Discuss. 228, 488 (2021).
- [24] K. Li, J. Laksman, T. Mazza, G. Doumy, D. Koulentianos, A. Picchiotti, S. Serkez, N. Rohringer, M. Ilchen, M. Meyer,

and L. Young, Ghost-imaging-enhanced non-invasive spectral characterization of stochastic x-ray free-electron-laser pulses, Commun. Phys. **5**, 191 (2022).

- [25] Y. Kayser, C. Milne, P. Juranić, L. Sala, J. Czapla-Masztafiak, R. Follath, M. Kavčič, G. Knopp, J. Rehanek, W. Błachucki *et al.*, Core-level nonlinear spectroscopy triggered by stochastic x-ray pulses, Nat. Commun. **10**, 4761 (2019).
- [26] P.-A. Moreau, E. Toninelli, T. Gregory, and M. J. Padgett, Ghost imaging using optical correlations, Laser Photonics Rev. 12, 1700143 (2018).
- [27] A. Schori and S. Shwartz, X-ray ghost imaging with a laboratory source, Opt. Express 25, 14822 (2017).
- [28] Y. Klein, O. Sefi, H. Schwartz, and S. Shwartz, Chemical element mapping by x-ray computational ghost fluorescence, Optica 9, 63 (2022).
- [29] O. Sefi, Y. Klein, E. Strizhevsky, I. P. Dolbnya, and S. Shwartz, X-ray imaging of fast dynamics with single-pixel detector, Opt. Express 28, 24568 (2020).
- [30] Y. Klein, A. Schori, I. P. Dolbnya, K. Sawhney, and S. Shwartz, X-ray computational ghost imaging with single-pixel detector, Opt. Express 27, 3284 (2019).
- [31] D. Pelliccia, A. Rack, M. Scheel, V. Cantelli, and D. M. Paganin, Experimental X-Ray Ghost Imaging, Phys. Rev. Lett. 117, 113902 (2016).
- [32] H. Yu, R. Lu, S. Han, H. Xie, G. Du, T. Xiao, and D. Zhu, Fourier-Transform Ghost Imaging with Hard X Rays, Phys. Rev. Lett. 117, 113901 (2016).
- [33] A. Schori, D. Borodin, K. Tamasaku, and S. Shwartz, Ghost imaging with paired x-ray photons, Phys. Rev. A 97, 063804 (2018).
- [34] Y. Y. Kim, L. Gelisio, G. Mercurio, S. Dziarzhytski, M. Beye, L. Bocklage, A. Classen, C. David, O. Yu. Gorobtsov, R. Khubbutdinov *et al.*, Ghost imaging at an XUV free-electron laser, Phys. Rev. A **101**, 013820 (2020).
- [35] D. Ratner, J. P. Cryan, T. J. Lane, S. Li, and G. Stupakov, Pump-Probe Ghost Imaging with SASE FELs, Phys. Rev. X 9, 011045 (2019).
- [36] F. Capotondi, E. Pedersoli, N. Mahne, R. H. Menk, G. Passos, L. Raimondi, C. Svetina, G. Sandrin, M. Zangrando, M. Kiskinova *et al.*, Invited article: Coherent imaging using seeded free-electron laser pulses with variable polarization: First results and research opportunities, Rev. Sci. Instrum. 84, 051301 (2013).
- [37] F. Capotondi, E. Pedersoli, F. Bencivenga, M. Manfredda, N. Mahne, L. Raimondi, C. Svetina, M. Zangrando, A. Demidovich, I. Nikolov *et al.*, Multipurpose end-station for coherent diffraction imaging and scattering at FERMI@Elettra free-electron laser facility, J. Synchrotron Radiat. **22**, 544 (2015).
- [38] E. Allaria, D. Castronovo, P. Cinquegrana, P. Craievich, M. Dal Forno, M. B. Danailov, G. D'Auria, A. Demidovich, G. De Ninno, S. Di Mitri *et al.*, Two-stage seeded soft-x-ray free-electron laser, Nat. Photonics 7, 913 (2013).
- [39] G. Penco, E. Allaria, G. De Ninno, E. Ferrari, and L. Giannessi, Experimental Demonstration of Enhanced Self-Amplified Spontaneous Emission by an Optical Klystron, Phys. Rev. Lett. 114, 013901 (2015).
- [40] L. Raimondi, C. Svetina, N. Mahne, D. Cocco, A. Abrami, M. De Marco, C. Fava, S. Gerusina, R. Gobessi, F. Capotondi *et al.*, Microfocusing of the FERMI@Elettra FEL beam with a K-B

active optics system: Spot size predictions by application of the WISE code, Nucl. Instrum. Methods Phys. Res., Sect. A **710**, 131 (2013).

- [41] R. Sobierajski, I. Jacyna, P. Dłużewski, M. T. Klepka, D. Klinger, J. B. Pełka, T. Burian, V. Hájková, L. Juha, K. Saksl et al., Role of heat accumulation in the multi-shot damage of silicon irradiated with femtosecond XUV pulses at a 1 MHz repetition rate, Opt. Express 24, 15468 (2016).
- [42] D. Gauthier, P. R. Ribič, G. De Ninno, E. Allaria, P. Cinquegrana, M. B. Danailov, A. Demidovich, E. Ferrari, L. Giannessi, B. Mahieu, and G. Penco, Spectrotemporal Shaping of Seeded Free-Electron Laser Pulses, Phys. Rev. Lett. 115, 114801 (2015).
- [43] P. Finetti, H. Höppner, E. Allaria, C. Callegari, F. Capotondi, P. Cinquegrana, M. Coreno, R. Cucini, M. B. Danailov, A. Demidovich *et al.*, Pulse Duration of Seeded Free-Electron Lasers, Phys. Rev. X 7, 021043 (2017).
- [44] S. Nannarone, F. Borgatti, A. DeLuisa, B. P. Doyle, G. C. Gazzadi, A. Giglia, P. Finetti, N. Mahne, L. Pasquali, M. Pedio et al., The BEAR Beamline at Elettra, in 1st International Conference on Achieving the Sustainable Development Goals, AIP Conf. Proc. No. 705 (AIP, Melville, NY, 2004), p. 450.
- [45] C. Li, W. Yin, H. Jiang, and Y. Zhang, An efficient augmented Lagrangian method with applications to total variation minimization, Comput. Optimization Appl. 56, 507 (2013).
- [46] A. Gatti, E. Brambilla, M. Bache, and L. A. Lugiato, Ghost Imaging with Thermal Light: Comparing Entanglement and ClassicalCorrelation, Phys. Rev. Lett. 93, 093602 (2004).
- [47] S. Hofmann, Auger-and X-Ray Photoelectron Spectroscopy in Materials Science: A User-Oriented Guide (Springer Science & Business Media, Berlin, 2012).
- [48] O. Y. Gorobtsov, G. Mercurio, F. Capotondi, P. Skopintsev, S. Lazarev, I. A. Zaluzhnyy, M. B. Danailov, M. Dell'Angela, M. Manfredda, E. Pedersoli *et al.*, Seeded x-ray free-electron laser generating radiation with laser statistical properties, Nat. Commun. 9, 4498 (2018).
- [49] O. Katz, Y. Bromberg, and Y. Silberberg, Compressive ghost imaging, Appl. Phys. Lett. 95, 131110 (2009).
- [50] S. Krinsky and Y. Li, Statistical analysis of the chaotic optical field from a self-amplified spontaneous-emission free-electron laser, Phys. Rev. E 73, 066501 (2006).
- [51] M. Veronese, R. Appio, P. Craievich, and G. Penco, Absolute Bunch Length Measurement Using Coherent Diffraction Radiation, Phys. Rev. Lett. **110**, 074802 (2013).
- [52] S. Krinsky and R. L. Gluckstern, Analysis of statistical correlations and intensity spiking in the self-amplified spontaneousemission free-electron laser, Phys. Rev. Spec. Top.–Accel. Beams 6, 050701 (2003).
- [53] S. K. Cushing, A. Lee, I. J. Porter, L. M. Carneiro, H.-T. Chang, M. Zürch, and S. R. Leone, Differentiating photoexcited carrier and phonon dynamics in the Δ, L, and Γ valleys of Si(100) with transient extreme ultraviolet spectroscopy, J. Phys. Chem. C 123, 3343 (2019).
- [54] S. Sastry, Illuminating liquid polymorphism in silicon, PNAS 107, 17063 (2010).
- [55] M. Beye, F. Sorgenfrei, W. F. Schlotter, W. Wurth, and A. Föhlisch, The liquid-liquid phase transition in silicon revealed by snapshots of valence electrons, PNAS 107, 16772 (2010).

References:

- 1. W. C. Röntgen, "On a new kind of rays," Science (80-.). 3, (1896).
- 2. "XIII. Polarised röntgen radiation," Philos. Trans. R. Soc. London. Ser. A, Contain. Pap. a Math. or Phys. Character **204**, (1905).
- 3. W. Friedrich, P. Knipping, and M. Laue, "Interferenzerscheinungen bei Röntgenstrahlen," Ann. Phys. **346**, (1913).
- 4. W. H. Bragg, "The reflection of X-rays by crystals," Nature **91**, 477 (1913).
- 5. J. D. Watson and F. H. C. Crick, "Genetical implications of the structure of deoxyribonucleic acid," Nature **171**, (1953).
- 6. H. G. J. Moseley, "XCIII. The high-frequency spectra of the elements," London, Edinburgh, Dublin Philos. Mag. J. Sci. **26**, (1913).
- 7. N. Bohr, "The spectra of helium and hydrogen [1]," Nature 92, (1913).
- 8. M. Siegbahn, "Relations between the K and L series of the high-frequency spectra [2]," Nature **96**, (1916).
- 9. A. Yonath, K. R. Leonard, and H. G. Wittmann, "A tunnel in the large ribosomal subunit revealed by three-dimensional image reconstruction," Science (80-.). **236**, (1987).
- 10. V. Cerantola, A. D. Rosa, Z. Konôpková, R. Torchio, E. Brambrink, A. Rack, U. Zastrau, and S. Pascarelli, "New frontiers in extreme conditions science at synchrotrons and free electron lasers," J. Phys. Condens. Matter **33**, (2021).
- P. Emma, R. Akre, J. Arthur, R. Bionta, C. Bostedt, J. Bozek, A. Brachmann, P. Bucksbaum, R. Coffee, F. J. Decker, Y. Ding, D. Dowell, S. Edstrom, A. Fisher, J. Frisch, S. Gilevich, J. Hastings, G. Hays, P. Hering, Z. Huang, R. Iverson, H. Loos, M. Messerschmidt, A. Miahnahri, S. Moeller, H. D. Nuhn, G. Pile, D. Ratner, J. Rzepiela, D. Schultz, T. Smith, P. Stefan, H. Tompkins, J. Turner, J. Welch, W. White, J. Wu, G. Yocky, and J. Galayda, "First lasing and operation of an ångstrom-wavelength free-electron laser," Nat. Photonics 4, (2010).
- 12. T. B. Pittman, Y. H. Shih, D. V. Strekalov, and A. V. Sergienko, "Optical imaging by means of two-photon quantum entanglement," Phys. Rev. A **52**, (1995).
- 13. J. H. Shapiro, "Computational ghost imaging," Phys. Rev. A 78, (2008).
- 14. T. J. Lane and D. Ratner, "What are the advantages of ghost imaging? Multiplexing for x-ray and electron imaging," Opt. Express **28**, 5898 (2020).
- 15. G. M. Gibson, S. D. Johnson, and M. J. Padgett, "Single-pixel imaging 12 years on: a review," Opt. Express 28, 28190 (2020).
- B. Sun, M. P. Edgar, R. Bowman, L. E. Vittert, S. Welsh, A. Bowman, and M. J. Padgett, "3D Computational Imaging with Single-Pixel Detectors," Science (80-.). 340, 844–847 (2013).
- 17. S. Ota, R. Horisaki, Y. Kawamura, M. Ugawa, I. Sato, K. Hashimoto, R. Kamesawa,

K. Setoyama, S. Yamaguchi, K. Fujiu, K. Waki, and H. Noji, "Ghost cytometry," Science (80-.). **360**, 1246–1251 (2018).

- 18. P. Janassek, A. Herdt, S. Blumenstein, and W. Elsäßer, "Ghost spectroscopy with classical correlated amplified spontaneous emission photons emitted by an erbium-doped fiber amplifier," Appl. Sci. 8, (2018).
- 19. P. Janassek, S. Blumenstein, and W. Elsäßer, "Ghost Spectroscopy with Classical Thermal Light Emitted by a Superluminescent Diode," Phys. Rev. Appl. 9, (2018).
- 20. C. Amiot, P. Ryczkowski, A. T. Friberg, J. M. Dudley, and G. Genty, "Supercontinuum spectral-domain ghost imaging," Opt. Lett. **43**, (2018).
- 21. S. Rabi, S. Meir, R. Dror, H. Duadi, F. Baldini, F. Chiavaioli, and M. Fridman, "Spectral Ghost Imaging for Ultrafast Spectroscopy," IEEE Photonics J. 14, (2022).
- S. Dongfeng, Z. Jiamin, H. Jian, W. Yingjian, Y. Kee, C. Kaifa, X. Chenbo, L. Dong, and Z. Wenyue, "Polarization-multiplexing ghost imaging," Opt. Lasers Eng. 102, (2018).
- 23. R. Baraniuk and P. Steeghs, "Compressive Radar Imaging," in 2007 IEEE Radar Conference (IEEE, 2007), pp. 128–133.
- 24. H.-C. Liu and S. Zhang, "Computational ghost imaging of hot objects in long-wave infrared range," Appl. Phys. Lett. **111**, 031110 (2017).
- 25. D. Shrekenhamer, C. M. Watts, and W. J. Padilla, "Terahertz single pixel imaging with an optically controlled dynamic spatial light modulator," Opt. Express **21**, 12507 (2013).
- 26. S. Li, F. Cropp, K. Kabra, T. J. Lane, G. Wetzstein, P. Musumeci, and D. Ratner, "Electron Ghost Imaging," Phys. Rev. Lett. **121**, 114801 (2018).
- R. I. Khakimov, B. M. Henson, D. K. Shin, S. S. Hodgman, R. G. Dall, K. G. H. Baldwin, and A. G. Truscott, "Ghost imaging with atoms," Nature 540, 100–103 (2016).
- 28. D. Pelliccia, A. Rack, M. Scheel, V. Cantelli, and D. M. Paganin, "Experimental X-Ray Ghost Imaging," Phys. Rev. Lett. **117**, 113902 (2016).
- 29. S. Eisebitt, J. Lüning, W. F. Schlotter, M. Lörgen, O. Hellwig, W. Eberhardt, and J. Stöhr, "Lensless imaging of magnetic nanostructures by X-ray spectro-holography," Nature **432**, (2004).
- 30. P. Thibault, M. Dierolf, A. Menzel, O. Bunk, C. David, and F. Pfeiffer, "High-resolution scanning X-ray diffraction microscopy," Science (80-.). **321**, (2008).
- 31. Y. Bromberg, O. Katz, and Y. Silberberg, "Ghost imaging with a single detector," Phys. Rev. A At. Mol. Opt. Phys. **79**, (2009).
- 32. O. Katz, Y. Bromberg, and Y. Silberberg, "Compressive ghost imaging," Appl. Phys. Lett. **95**, (2009).
- 33. M. Lyu, W. Wang, H. Wang, H. Wang, G. Li, N. Chen, and G. Situ, "Deep-learning-based ghost imaging," Sci. Rep. **7**, 17865 (2017).
- 34. P. Sedigh Rahimabadi, M. Khodaei, and K. R. Koswattage, "Review on applications

of synchrotron-based X-ray techniques in materials characterization," X-Ray Spectrom. **49**, 348–373 (2020).

- 35. M. Maiuri, M. Garavelli, and G. Cerullo, "Ultrafast Spectroscopy: State of the Art and Open Challenges," J. Am. Chem. Soc. **142**, 3–15 (2020).
- 36. C. Li, W. Yin, H. Jiang, and Y. Zhang, "An efficient augmented Lagrangian method with applications to total variation minimization," Comput. Optim. Appl. **56**, 507–530 (2013).

<u>תקציר</u>

חישה באמצעות קרני רנטגן היא כלי שימושי ביותר למדע בסיסי, תעשיית ההיי-טק, רפואה, אבטחה ועוד מגוון רחב של תחומים. היכולת של קרני הרנטגן לחדור לעומק החומר מאפשר ניטור של עצמים שבכל תחום אחר הם בלתי נראים. נוסף לכך, בזכות האנרגיה הגבוהה ואורך הגל הקצר שלהן ניתן לנתח אלמנטים פנימיים ברזולוציה אטומית. עם זאת, המדידה בתחום הזה מאתגרת. ייצור של רכיבים אופטיים כמו עדשות ומראות הוא מורכב בשל מקדם השבירה הנמוך מאוד בטווח זה.

בעבודת הדוקטורט שלי, פיתחתי שיטות הדמיה וספקטרוסקופיה חדשות המשפרות את הביצועים של הטכניקות הסטנדרטיות. השתמשתי בחישה קורלטיבית, שמבוססת על מדידה על ידי פיקסל בודד וחישובי קורלציה. בניסויים שונים שביצעתי, הדגמתי את היתרונות של שיטה זו דווקא בתחום הרנטגן.

ראשית, בתחום הדימות, הדגמתי בפעם הראשונה חישה קורלטיבית ללא צורך במצלמה. ניסוי זה הראה את היתרון של חישה קורלטיבית בהיבט של רזולוציה מרחבית, בכך שהרזולוציה נקבעת רק על ידי גודל תבנית במסכה. טכניקה זו פותחת את האפשרות לדימות רנטגן ברזולוציה גבוהה באמצעות מערכת פשוטה ופרקטית, כפי שפורט במאמר הראשון שלי.

בניסוי השני שלי פיתחתי שיטה לדימות פלואורוסנטי. מדדתי פליטה במקום העברה ועל ידי כך יכולתי לבצע מיפוי דו ממדי של אלמנטים כימיים. בהשוואה לטכניקה הסטנדרטית המבוצעת באמצעות סריקה, השיטה שלי מאפשרת שיפור ברזולוציה, ובנוסף, על ידי שימוש באלגוריתמים של חישה דחוסה ניתן גם להפחית משמעותית את זמן המדידה. במאמר השני שלי, הדגמתי שאפילו עם מספר סריקות קטן פי עשר ממספר הפיקסלים שבתמונה, ניתן לשחזר במדויק את התמונה הכימית. יכולת זו מאפשרת מיפוי כימי מהיר ויעיל.

המאמר השלישי שלי מתמקד בהדגשת היתרון של חישה קורלטיבית כאשר ישנו רעש מובנה במערכת. ספקטרוסקופיה בלייזר רנטגן היא תחום מוביל ורלוונטי ביותר, המאפשר ניטור של תהליכים מאד מהירים ברמה האטומית. עם זאת, שינויים ספקטרליים בין הפולסים של הלייזר מקשה מאד על מדידת הספקטרום. בניסוי שלי, הראיתי שניתן להשתמש בווריאציות האלו לביצוע חישה קורלטיבית בתחום הספקטרלי. כך, ניתן לבצע מדידות ברזולוציה ספקטרלית גבוהה ובזמן קצר. טכניקה זו, המשלבת מערכת פשוטה עם יכולות יוצאות דופן, מאפשרת מדידת אפקטים בחזית המחקר שטרם נמדדו.

לסיכום, השימוש בחישה קורלטיבית מציע יתרונות רבים בתחום הרנטגן. הניסויים שביצעתי בדימות וספקטרוסקופיה, יכולים להפוך לכלים רבי עוצמה למדידת אפקטים שלא נמדדו עד היום.

א

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דימות וספקטרוסקופיה בתחום קרני הרנטגן על ידי גלאי בעל פיקסל בודד

חיבור לשם קבלת התואר ״דוקטור לפילוסופיה״

מאת:

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המחלקה לפיסיקה

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