Multiple-Energy X-ray Holography with Atomic Resolution

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Multiple-energy x-ray holography (MEXH) is a particular implementation of an x-ray holographic method capable of directly imaging atomic structures in the bulk, at surfaces and interfaces of solids. It utilizes an interference field generated by incident and scattered x-rays within the sample, then determines its strength at specific atomic sites from integral fluorescence yields. Scanning large portions of reciprocal space, a hologram is recorded, which can be converted to a real space image by Fourier transformation. Image aberrations that adversely affect results in single-energy techniques are successfully avoided in this novel multi-energy version.

KEYWORDS: x-ray holography, electron holography

1. Introduction

The discovery of holography by Gabor\(^1\) in 1948 introduced a way to directly image three-dimensional structures, and although atomic resolution was not achieved in Gabor's time, this novel technique lead to numerous applications in various scientific, technical and non-scientific fields. In recent years it had been pointed out that interference patterns generated by radiation from atomic sources inside a solid, e.g. photoelectrons, Auger electrons, or fluorescence, can be thought of as a holographic record from which meaningful real-space images can be reconstructed\(^2\). Holographic imaging algorithms for both single- and multiple-energy measurements were put forth\(^3\) and were first verified experimentally by electron emission holography\(^6\)\(-\)12\), which, in the meantime, shows considerable promise as a new surface structural probe. In particular, the virtue of multiple-energy measurements as a straightforward way to avoid image aberrations has been well established in photoelectron holography, where the energy of the emitted photo-electron can be varied by changing the energy of the incident beam.

For x-rays, these holographic ideas are equally if not more attractive. The isotropic nature of the reference and scattering wave fronts, the absence of strong multiple scattering and the longer mean free path make x-rays a versatile probe for bulk, surface and especially buried interface investigations. Two experimental variations of the same principle, x-ray fluorescence holography (XFH)\(^13\) and multi-energy x-ray holography (MEXH)\(^15\) have been proposed and successfully applied to various bulk samples.

Using XFH, fluorescence from atoms inside the sample is excited by suitable ionizing radiation, such as x-rays, electron- or ion- beams. Interference between fluorescence from the sample reaching a detector in the far field directly and fluorescence being elastically scattered by atoms in the sample first, then reaching the detector, contains holographic information. When recorded for all directions of reciprocal space, it constitutes a single-energy hologram which can be inverted by Fourier transform to yield a real-space image of the atomic distribution in the sample. A first image of SrTiO\(_3\) as acquired by XFH has been reported\(^14\).

With MEXH, tunable, monochromatic synchrotron radiation is used to generate an interference field between incident and elastically scattered waves inside the sample. When scanning the incident wave vector over all of reciprocal space, a measurement of this field constitutes a complete hologram, which can be Fourier inverted to yield a real-space image. To map-out this field, fluorescence, which is proportional to the interference field at the position of the generating atom, is recorded externally. It has to be emphasized here, that MEXH utilizes fluorescence as a detector for the hologram generated at the incident energy, whereas in XFH fluorescence itself constitutes the hologram.

By virtue of the optical reciprocity theorem, the two x-ray holography schemes described above are equivalent when used at one energy only. However, some practical aspects make one or the other more advantageous in particular cases. MEXH offers tunability of the incident beam and the opportunity to collect data sets at multiple energies. It enables sampling of a more complete volume of reciprocal space and thereby avoids image aberrations, holographic twin images, multiple scattering\(^4\) and accidental image cancellations which can drastically distort single energy holograms. XFH in turn uses unpolarized fluorescence in steady of linearly polarized synchrotron radiation. Therefore it is insensitive to varying scattering amplitudes for atoms in different directions from the detector atom. MEXH will have to turn to circularly polarized light or independent measurements for orthogonal polarizations to alleviate this problem.

Applications for x-ray holography are envisioned to include imaging of solid state surfaces, buried interfaces, defect sites in bulk crystals and other structures involving dilutes constituents such a nano-crystals, atomic clusters and maybe even biological samples.

2. X-Ray Holography

In order to explain the mechanism that leads to the X-ray hologram and a real space reconstruction of an atomic structure, a comparison with ordinary optical holography is invoked. In general, holography attempts to record a wave field surrounding an object to be imaged in such a complete fashion that no visual distinction exists between the original object and its holographic reconstruction. This is accomplished by measuring not only the intensity of beams emerging from the object, as is done in regular photography,
but also the phase of every partial object beam with respect to some fixed reference. A generic set-up for off-axis holography is shown in Fig. 1. Light from a coherent source is divided into two portions by a beam splitter. The first, which is made to diverge by a suitable lens, illuminates the object, generating reflected and scattered object beams from various parts of the sample, the second stays unobstructed to serve as the phase reference. Due to the difference in path lengths that object beams encounter, their relative phases differ accordingly. To determine these phases, object beams are allowed to interfere with the reference beam, thus encoding the phase information in the degree of constructive or destructive interference. The resultant intensity distribution is recorded on photographic film. To reconstruct the holographic image, a duplicate of the original reference beam is shone onto the hologram and the image appears in a three-dimensional 'life-like' fashion at its original position. There it can be viewed from an angular range that is identical to the divergence of the original illuminating beam.

![Fig. 1. Ordinary optical off-axis holography. A coherent beam of light is divided into two portions by a beam splitter. The first illuminates the object to be imaged, thus generating scattered object beams. The second serves as a phase reference. Interferences between object beams and the phase reference comprise the hologram and are recorded on photographic film. A holographic reconstruction is achieved by shining the original reference beam onto the hologram.](image1)

The generation of an X-ray hologram using the MEXH scheme proceeds in very much the same way. As shown in Fig. 2, a coherent X-ray beam is incident on a group of atoms. The portion which does not interact at all with any atom will serve as the phase reference. Portions which are scattered by neighboring atoms surrounding a designated 'detector atom' comprise the object beams. Interference of these object beams with the phase reference results in an electric field strength which gives rise to a proportional generation of fluorescence at the position of the detector atom. By integrally recording this fluorescence emitted into all directions, an external measure for the in-situ interference field is readily available. Since the incident X-ray beam is ideally collimated or covers only a small angular range in practice, illumination of the sample from all sides has to be done successively. This means, that the incident wave vector has to be scanned over all of reciprocal space. The recorded fluorescence intensity $I_F(k)$ is then equivalent to the hologram, stored on photographic film in the regular optical case.

![Fig. 2. Multiple-energy X-ray holography. A coherent, monochromatic X-ray beam is incident on a group of atoms to be imaged. Unscented radiation serves as a phase reference, scattered radiation comprises the object beams. The intensity of the in-situ interference field is measured by integrally recording fluorescence from the detector atom. Scanning $k$ for all of reciprocal space leads to a complete hologram, which can be inverted by Fourier transformation to yield a real-space image.](image2)

A holographic reconstruction of a real-space image from an X-ray hologram is not quite as easy as in the optical case. Distances to be imaged are so small that, even if it existed, a direct visual image would be of no avail. Instead, the help of a numerical technique and a computer has to be enlisted to convert the hologram into an image. As will be shown in more detail below, incident wave vectors $k$ and the atomic coordinates $R_i$ within the sample form a conjugate Fourier pair, transition between which is mediated by a Fourier transformation. Thus a real-space image of the atomic distribution inside the sample as seen from the position of the detector atom is achieved in principle by Fourier transformation of the X-ray hologram.

3. Theory

To put the mechanism of generating an X-ray hologram and a real space reconstruction on a more solid footing, a simple theory is briefly reviewed here. The X-ray hologram emerging from a MEXH measurement consists of a determination of the electric field at the position of a particular 'detector atom' inside the sample, as it arises through a superposition of the incident beam with scattered beams from neighboring atoms and as it fluctuates when the incident wave vector is scanned over an extended volume of reciprocal space. This electric field for a detector atom at $r$ as a function of $k$ can be written as:
\[ \mathbf{E}(\mathbf{k}) = \mathbf{E}_{\text{incident}} + \sum_j \mathbf{E}_{\text{scatter}} \]

\[ = E_0 \mathbf{p} e^{i \mathbf{k} \cdot \mathbf{r}} + \sum_j E_0 |f(\theta)| e^{i\Phi} \mathbf{F}_P \frac{1}{R_j} e^{i(\mathbf{k} \cdot \mathbf{r} - \mathbf{k} \cdot \mathbf{R}_j - \mathbf{k} \cdot \mathbf{k} \cdot \mathbf{R}_j)} \]

where the summation extends over all atoms of the sample. The vector \( \mathbf{p} \) designates the polarization of the incident beam, while \( \mathbf{P} \) describes the projection of this vector onto the scattering plane comprising the current wave vector \( \mathbf{k} \) and a scatterer \( j \). The exponent (\( \mathbf{k} \cdot \mathbf{r} - \mathbf{k} \cdot \mathbf{R}_j \)) arises from the geometric path difference between the incident beam and a beam reaching the detector via scattering from a neighboring atom and includes the coordinates \( \mathbf{R}_j \) of every atom with respect to the detector. It is these structure-determining \( \mathbf{R}_j \) of course that one would like to extract by Fourier transformation from the hologram as the final result of the measurement. The function \( |f(\theta)| e^{i\Phi} \) is a generalized scattering amplitude, which for X-rays far from an absorption edge can often be treated as a purely real function. For electrons or for X-rays close to an edge, however, the scattering phase will mix with the geometric phase and will directly obscure the resulting coordinates \( \mathbf{R}_j \). In cases where \( \Phi \) cannot be neglected, an independent method of determination or a model calculation has been to employ to separate the phases and retrieve a high fidelity holographic reconstruction.

The quantity measured when recording fluorescence, however, is not the electric field but its intensity, which by virtue of Eq. (1) is proportional to

\[ I_{\mathbf{k}}(\mathbf{k}) \propto \mathbf{E}(\mathbf{k}) \cdot \mathbf{E}(\mathbf{k}) \]

\[ = I_0 \left[ |\mathbf{P}|^2 + 2 \sum_j (\mathbf{p} \cdot \mathbf{P}) |f(\theta)| \frac{1}{R_j} e^{i(\mathbf{k} \cdot \mathbf{R}_j - \mathbf{k} \cdot \mathbf{R}_j)} \right] + |\mathbf{P}|^2 |f(\theta)|^2 \sum_j \frac{1}{R_j} e^{i(\mathbf{k} \cdot \mathbf{R}_j - \mathbf{k} \cdot \mathbf{R}_j)} \]

With \( |f(\theta)| \) rather small, the second term represents an equally small modulation of an overwhelming background given by the first term. The third term is appreciable only near a strong Bragg reflection.

Having measured the fluorescence intensity, the hologram \( \chi(\mathbf{k}) \) is retrieved by subtracting the constant background

\[ \chi(\mathbf{k}) = \frac{I_{\mathbf{k}}(\mathbf{k}) - I_0}{I_0} \]

In this context, detector efficiency and absorption corrections are usually also taken into account. If the hologram was determined for all reciprocal space, a straightforward Fourier transformation

\[ U(\mathbf{r}) = \int d^3k \chi(\mathbf{k}) e^{-i \mathbf{k} \cdot \mathbf{r}} \]

would lead to the real-space reconstruction \( U(\mathbf{r}) \). Since a complete hologram cannot possibly be accomplished, the Helmholtz-Kirchhoff theorem\(^{17,3,4,23} \) has to be called to the rescue. It states that a real-space reconstruction can already be extracted from a hologram that is determined only for a spherical shell in reciprocal space,

\[ U_k(\mathbf{r}) = \iiint \chi(\mathbf{k}) e^{-i \mathbf{k} \cdot \mathbf{r}} \frac{1}{|k|^2} \cos \theta \, d\theta \, d\phi \]

hence a useful X-ray holography measurement can be conducted even for a single photon energy, where \( |k| \) is constant. The price one has to pay, however, manifests itself in quite drastic image distortions and the well-known twin images. These defects can successively be avoided by repeating measurements at multiple energies and performing a 'phased summation'

\[ U(\mathbf{r}) = \sum_j U_k(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}} \Delta k \]

The possibility of combining multiple single-energy holograms into one improved multiple-energy hologram is the principle advantage of MEXH.

4. Experimental Set-up

The experimental set-up for a MEXH experiment aims to measure fluorescence from the sample while scanning the incident wave vector in spherical coordinates. The sample is mounted at the center of a six-circle diffractometer (Fig. 3) in such a way that a rotation \( \Phi \) around its surface normal and a variation in inclination angle \( \Theta \) correspond to the two angular coordinates, while the energy of the incident beam determines \( |k| \). Coherent radiation is derived from a double bounce monochromator, which may be equipped with either crystals or multilayers. The amount of longitudinal coherence length available is determined by the degree of monochromaticity, but since MEXH at this stage is concerned with only very short distances between a detector atom and neighboring scatterers, typically 30 Å or less, even a multilayer will provide sufficient longitudinal coherence while drastically increasing photon flux through its greatly enhanced band pass. Transverse coherence length is determined by the characteristics of the synchrotron radiation source, but again, even a conventional X-ray tube is coherent enough for the purpose of imaging closest neighbors.

Of great concern is the fluorescence detection system. It must have as large an acceptance angle as possible, not only to increase the count-rates, but also to average over an inhomogeneous distribution of fluorescence as it is created by the presence of Kossel lines in crystalline samples\(^{18} \). A cylindrical graphite analyzer with a succeeding proportional counter was chosen for its ability to finely discriminate fluorescence energy while having large count-rate capability\(^{19} \). The angular acceptance of the analyzer was approximately 0.016 sr, only one thousandth of the entire half sphere above the sample but large enough to provide
averaging of the fluorescence field and suppress its local structure.

Fig. 3. Experimental configuration for MEXH measurements. Monochromatic synchrotron radiation is incident on the sample, which is moved in terms of the inclination angle $\Theta$ and the azimuthal angle $\Phi$ to scan an extended volume of reciprocal space. Fluorescence is collected by a curved graphite analyzer and proportional counter. A typical $\Phi$-scan is shown in the insert. The signal modulation is typically 0.1-0.5% of the total number of counts, on an otherwise constant background.

5. Measurements

The first successful MEXH experiment was conducted at the Oak Ridge National Laboratory beamline X-14A at the National Synchrotron Light Source of Brookhaven National Laboratory$^{15}$. The sample was a natural slab of hematite (Fe$_2$O$_3$) with a surface normal parallel to the (001) direction. The crystal structure of hematite can be conveniently described in a hexagonal system. Viewed along the c-axis, it consists of alternating layers of iron and oxygen atoms, where iron layers in themselves are separated into two distinct planes spaced about 0.6 Å apart. MEXH cannot distinguish between the different iron layers, therefore a superposition of both structures is expected in the holographic reconstruction, resulting in six apparent nearest neighbors for every Fe atom.

About 1500 data points for fluorescence intensities were collected in the hemisphere above the sample at three incident energies, 9.00, 9.65 and 10.30 keV. Fluorescence data from a typical $\Phi$-scan are shown in the insert of Fig. 3 showing a modulation of the integrated field with an amplitude of about 0.5% on a rather large constant background. Using algorithms as outlined above, a real-space atomic image was obtained for a (001)-plane passing through an Fe atom. It is shown in Fig. 4 and closely matches the expectations. An attempt was made to also reconstruct a (110) plane, but only few of the Fe atoms were visible. This is attributed to a loss of image resolution along the c-axis as a direct consequence of the limited range of energy and solid angle available in this first experiment.

Since then, various other samples have been studied successfully with MEXH by research groups world-wide, Ge$^{16}$, Cu$_3$Au$^{20}$ and Zn:GaAs$^{21}$ to name just a few.

Fig. 4. Holographic reconstruction of a (001) Fe double layer of hematite. Visible are the six possible nearest neighbors to the center atom at distances of 2.9 Å. Corner atoms on the hexagonal base grid can be identified up to a distance of 8.7 Å.

GaP clusters in Si

To extend the class of subjects accessible with MEXH to samples with very small concentrations of fluorescing atoms and to make the transition from well-known bulk crystal structures to materials that cannot be studied so readily with established methods, a hologram of small GaP clusters suspended in a Si matrix was attempted. The samples were made by ion beam synthesis$^{22}$ and GaP clusters were expected to be roughly oriented along the host Si lattice, maintaining their basic zincblende structure. The measurements were carried out at beamline X25 of the NSLS, using a multilayer monochromator as the source of incident radiation. Preliminary results indicate that measured signals were sufficiently strong to yield meaningful images. A first reconstruction of the (001) plane at $z = 0$ and $z = 1/2a$, shown in Fig. 5, suggests that the structure of GaP clusters is indeed of the zincblende type. More measurements are necessary, however, to fully determine the atomic arrangement in this particular sample for both Ga and the lighter-weight P.

6. Conclusion

While these first MEXH results are very encouraging, several issues have to be addressed before this method can be promoted into the sphere of routine analytical tools. The data acquisition time for a complete X-ray hologram, which
was of the order of 150 hr in the first experiment has to be reduced by increasing the incident flux and, more importantly, by developing a detector that covers a substantially larger solid angle than is covered at present. For MEXH the polarization issue has to be studied by using circular polarization or combining independent measurements with orthogonal polarization. More theoretical work has to be done to refine the reconstruction procedures and samples with even lower concentration of fluorescing atoms have to be dealt with to break into the domain of surfaces, interfaces and biological samples.

Fig. 5. Holographic reconstruction of GaP clusters in Si.
Top: schematic structure of the sample; bottom left: (001) plane at z=0; bottom right: (001) plane at z=1/2a.

Nonetheless, the results presented above demonstrate that multiple-energy X-ray holograms are feasible and that this method shows promise of becoming a powerful new tool for directly imaging atomic structures in the bulk or at surfaces and interfaces of solids.

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