X-ray fluorescence holography

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Abstract

X-ray Fluorescence Holography (XFH) is a developing technique to image 3-dimensional clusters not requiring translational periodicity. It consists in measuring the fluorescent yield of an atomic species as a function of the direction of the detector (normal XFH) or as a function of the incident beam direction (inverse XFH).

Recent experimental results are illustrated. A significant improvement in the image quality compared to previous demonstration experiments was obtained. Further improvements in the experimental setup and data analysis are discussed including the requirements for X-FEL based experiments.

1 Introduction

For most of this century physicists have looked for ways to peer inside solids and learn the positions of atoms. While techniques such as x-ray and neutron diffraction have been successful for many decades, they have shortcomings: they work best on large, high quality crystals, which are hard to grow for many materials and impossible for others. And diffraction methods record only the intensity of scattered radiation, not the phase, which adds an additional layer of complexity for interpretation.

In 1996 a new method, the atomic resolution x-ray holography emerged. It is based on the holographic imaging technique, invented by Gabor 50 years ago [1].

Holography is a technique that allows to record both the phase and the intensity of a scattered wave. This is done by recording the interference pattern between an object wave and a well-known reference wave.

Another advantage of holography compared to diffraction, is that it works with arbitrarily small samples, down to a single molecule, as long as the sample provides enough signal to allow the recording of a hologram before its destruction.

2 Holography with inside source or detector

There are basically two kinds of holography, one using as a reference wave a plane wave and one using a spherical wave, although more complex waves have been used. If we use

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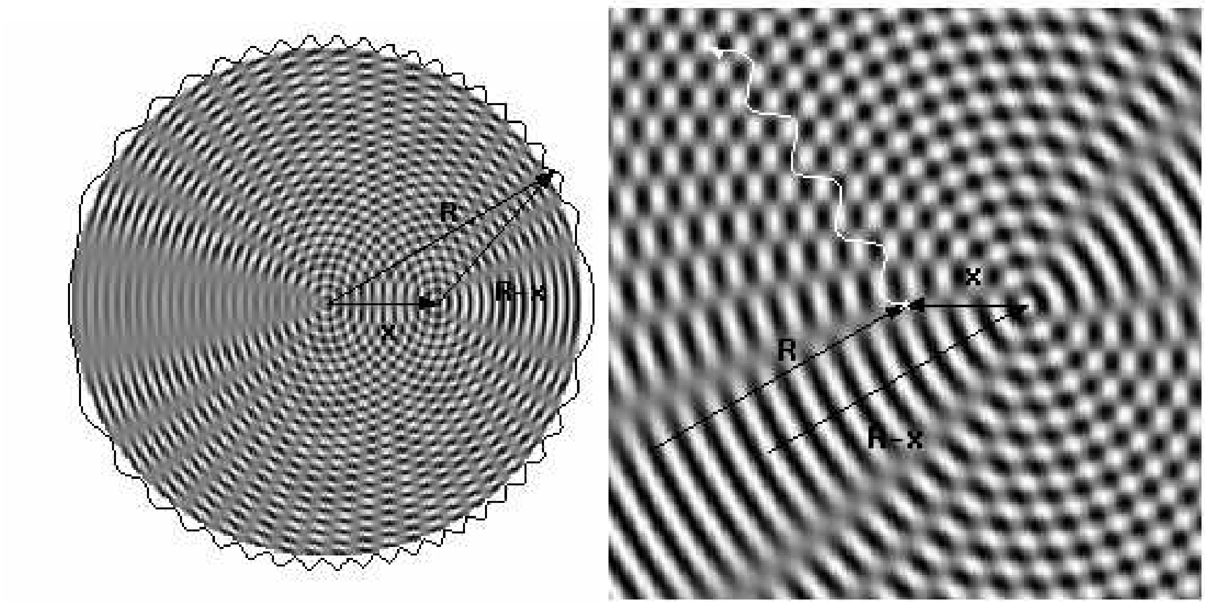

Figure 1: Inside source (left)-Inside detector holography

the plane wave we can put the detector in the near field of the object, the object will produce a phase shift in the plane wave, without significant deviation from the forward direction (near field condition). The propagation of the object wave does not produce any magnification, and the resolution is limited by the detector. If the detector is in the far field (*i.e.* Gabor holography), the object wave will be the Fourier transform of the wave in the near field, higher spatial frequencies diffract at higher angles. The highest spatial frequency of the object that can be reconstructed is then limited by the maximum scattering angle measured. There are two factors that limit the scattering angle that can be measured: the coherence of the source and the detector resolution (at high angles the interference pattern has spatial frequency of the order of the wavelength). A spherical reference wave overcomes the detector resolution problem, but this time the resolution is limited by how precisely the source location is determined, one cannot see something smaller than the source size.

This problem can be partially solved by using the atoms or nuclei of the sample as sources or detectors. This idea is called the "inside source" or "inside detector" concept.

Consider an atom in an excited level emitting some kind of radiation in form of a spherical wave. This wave is our reference beam. The wave scattered by the surrounding atoms will be the object wave. The interference pattern formed far from the source has all the ingredients to be used as a hologram.

The first experimental realisation of the inside source concept was reported in 1974 [2]. Bartell and co-workers used electrons scattered by the nuclei of a partially oriented gas as reference waves. They could image the atomic electron cloud with a resolution of 0.08 Å. However, they could only study monatomic gases and small molecules using their experimental arrangement.

Szöke suggested ten years later [3] that instead of making the hologram with a single molecule, one could take many molecules with the same orientation so that they all form the same hologram. A system satisfying this property is a crystal.

This idea was applied to all sort of particles emitted by an atom, photoelectrons, spin polarised photoelectrons, Auger, quasielastic (Kikuchi), Diffuse LEED, electron-energy-loss spectroscopy, x-rays and γ-rays [4]. Even sound waves emitted by a wale were used to recover the location of the surrounding wales [5].

While the scattering from atoms is much weaker and more isotropic for x-rays than for electrons, producing less aberration in the holographic process, the application of hard x or γ rays for holographic imaging was delayed. The main reason is the same that makes x-ray a more ideal case for holography: the weak scattering factor produces a very small signal, it is necessary to collect about 10^{10} photons to image relatively heavy (*e.g.* Fe) first neigbours of the emitting atom.

In 1996 using careful experimental arrangements, the 3D order of Sr atoms was reconstructed in $SrTiO_3$ [6] using K_α x-ray photons from Sr atoms.

Few months later the inside detector concept was published together with the experimental results [7]: the 2D picture of the Fe atoms in the basal plane of Fe_2O_3.

We know from the optical reciprocity principle that if we invert the time, and exchange detector with the source, we obtain the same experiment. Now we have a source in the far field- Fig. 1, producing a plane wave impinging on the sample. This plane wave is scattered by the atoms producing an interference pattern inside the sample. If an atom can be excited by this radiation, it will have higher/lower probability of being excited if the interference between the plane wave and the scattered waves is constructive/destructive at its location. Decay process such as the fluorescent yield is thus a measurement of the field amplitude inside the sample on the 'detector' atom position. We know from optical reciprocity that this measurement gives exactly the same information as the *normal* hologram, except the fact that the wavelength used in this experiment is given by the incoming plane wave and not by the emitted radiation.

Practically the difference between the inside source/inside detector holography methods is that the inside source holography is a *normal* holography: there is a source, an object and we could record a hologram on an ideal film selecting,with good linearity, only the photons emitted by the source. The other method with inside source is the *inverse*, or reciprocal: we have to move the source (x-ray beam) with respect to the sample. The main advantage is that we can choose the wavelength and record the inverse holograms at several wavelengths. For this reason the latter is well adapted to synchrotron sources, where one can tune the photon energy, but is not suited to an FEL source if one wants to record a hologram with a single bunch, since the recording requires to rotate the sample.

3 Results

In a recent experiment [8] carried out at the European Synchrotron Radiation Facility (Grenoble) on the ID18 undulator beamline with a Si (111) double crystal monochromator we obtained a significant improvement in the image reconstruction quality.

The experiment consisted in measuring precisely the fluorescent yield as a function of the direction of the incoming beam, to detect an oscillating signal of 10^{-3} with respect to the almost isotropic fluorescence. The detector system consist of an Avalanche Photo Diode that can handle a few MHz count rate, and a doubly focusing crystal analyser of pyrolitc graphite [9], to focus and discriminate the photons before they reach the APD. The acquisition of a hologram took 3 hours, $5.5\,10^{10}$ points with 10^6 photons per point. The sample was a CoO (111) crystal with mosaic spread of 0.3^o degree, shaped as a circular platelet with about 1 cm diameter and 1 mm thickness. It has a face centered

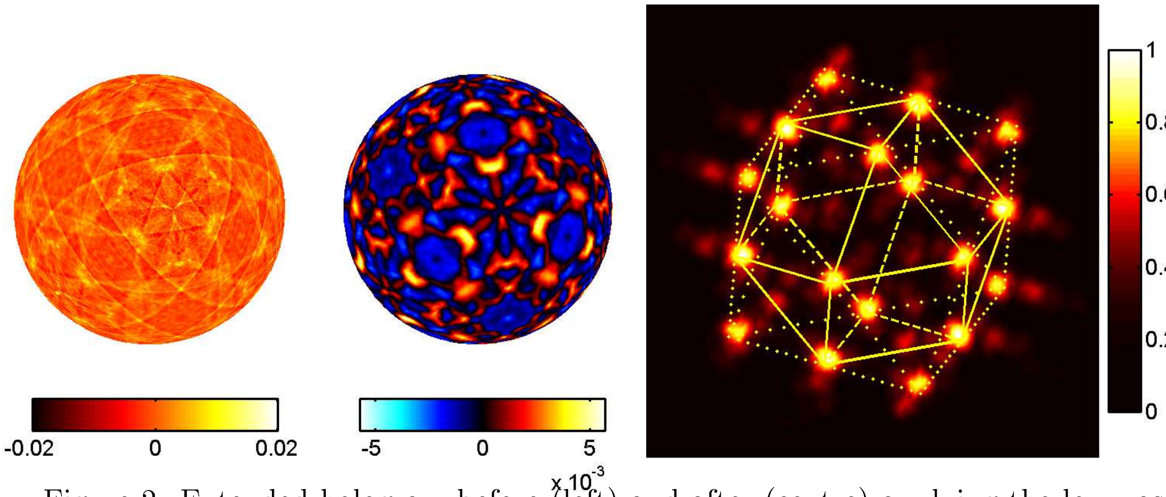

Figure 2: Extended hologram before (left) and after (centre) applying the low pass filter. (right) Reconstructed 3D image of the Co atoms. Solid and dashed lines show the first neighbour cluster, dotted lines point to second neighbour positions. Phis. Rev. Lett **82** (1999) 4847.

cubic structure with lattice parameter a=4.26 Å. The measurement described here is holography in inverse mode with energy E = 13.861 KeV. The raw data is dominated by the absorption dependence of the flat sample. This dependence can be easily calculated and corrected by fitting an analytical expression. The remaining sharp line pattern is due to x-ray standing waves (XSW), produced by the long-range periodic order present in the sample. Beside the lattice spacing, and atomic decoration, these patterns also reflect the crystal symmetry. We used this symmetry to extend the measured data into the full solid angle as shown in Fig. 2, which shows a projection of the hologram measured on a sphere. The standing waves pattern contains no phase information and these lines have a larger amplitude than the holographic signal. The XSW can be filtered out by a low pass spatial filter. After that, the intensity distribution contains only the holographic information. The 3D image reconstructed from this hologram was performed by applying the Helmoltz- Kirchhoff integral. This image together with the outline of the crystal lattice is presented in Fig. 2. Not only the 12 first Co neighbours, but also the 6 second Co neighbours can be clearly seen. The approximately 0.5 Å FWHM reflects the experimental resolution. Of course, the positions of atoms can be determined more accurately by taking the maximum of the intensity distribution. The deviation of the intensity maxima from the expected positions of the first Co neighbors is less than 0.1 Å.

4 Possible improvements

The measurement performed in about 3 hours is still far from the optimal experiment that could be obtained at a synchrotron source:

- The detector was collecting through a focusing crystal analyser only a small part of the full yield ($\sim 10^{-3}$). We improved our crystal analyser [9] to collect a 4 times larger solid angle, the remaining limitation being now the APD saturation. The ideal detector both for normal and inverse holography should collect the yeld over the full solid angle, and in case of normal holography with an angular resolution of about $2^o \times 2^o$. Developments in this direction are under study [11], using arrays of energy discriminating Si drift detectors. But the problem of such kind of detectors is that they cannot accept more than one photon per electron bunch. To overcome this problem, the energy discrimination should be performed before the photons reach the detector; for instance using an array of crystal analysers.

- The source being used (undulator source with Si(111) double crystal monochromator) is far better in terms of energy resolution than what really necessary: if we want to image only neighbours within a few nm from the 'detector' atom, we need just a comparable coherence length. Ideally one can increase the bandwidth by two orders of magnitude.

- Data analysis: up to now the reconstruction algorithm that calculates the wave-field intensity of the x-rays around the source, basically a kind of Fourier transform, produces artefacts in the real space image covering light atoms and far neighbours. This is due to the fact that part of the information in the reciprocal space is not known and assumed to be zero. Moreover the reconstruction algorithm does not take into account the anisotropy of the scattering and the *ghost image* problem of holography. Iterative methods, through minimization of χ^2 with some regularisation (*e.g.*maximum entropy) although quite CPU demanding should reduce the artefacts.

5 Conclusion

X-ray holography with inside source or detector is in the early stages of development. Although significant improvements from the demonstration experiments have been performed, the ideal setup for synchrotron radiation experiments is still ahead; moreover further developements in the data analysis is required before the the real capabilities of the method could be assessed.

Extrapolating the results from synchrotron radiation sources to an X-FEL source, it should be possible to record a hologram within a single bunch, provided that the sample has enough fluorescing atoms and that the proper detector system is developed. To image a sample with less then 10^{10} fluorescent atoms within a single FEL pulse one has to address to other techniques[2].

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