X-ray and γ-ray Holography Improve Views of Atoms in Solids

New developments make possible the imaging of light atoms and the removal of image distortions.

Dennis Gabor invented holography in 1948 in an attempt to extract atomic-resolution information from electron microscopy. Most standard diffraction techniques are sensitive only to the amplitude of the field; any information stored in the field's phase is lost. Gabor proposed mixing the wave that has passed through a sample with a reference wave; the resulting interference pattern contains both phase and amplitude information and leads directly to the three-dimensional structure.

Although optical and electron holography have by now become commonplace, they have their limitations. In optical holography, the resolution is restricted by the wavelength of the light to several hundred nanometers. Lens aberrations in electron microscopes have prevented the achievement of atomic resolution in electron holography. In addition, the strong electron interactions in solids complicate extracting information from the holographic interference pattern and confine application of low-energy electron holography to surface studies.

In contrast, the short wavelengths of hard x rays and γ rays (on the order of 1 Å) offer the potential for obtaining atomic resolution from the bulk. Furthermore, x rays are only weakly scattered in solids, which simplifies the interpretation of the images. Whereas x-ray diffraction relies on the long-range translational periodicity, x-ray and γ-ray holography are local methods that image the environment around selected atoms. Recent advances in x-ray and γ-ray holograms are increasing their information content, improving the quality of the reconstructed images, and allowing the imaging of light atoms and noncrystalline and doped samples.

From the inside out

X-ray holography initially presented a greater challenge to experimenters than optical or electron holography because of the difficulty of obtaining an x-ray source with sufficient coherence. Without good coherence, the phase information is washed out. Also, for atomic resolution, the position of an external source must be stable with respect to the sample to within an angstrom. An elegant solution to these difficulties was proposed 15 years ago by Abraham Szöke at Lawrence Livermore National Laboratory: Use atoms or nuclei within the sample as the source.[1]

First implemented for holography with photoelectrons and Auger electrons, the technique also works with x rays and γ rays.[2] Figure 1a illustrates the concept. Within a sample, atoms stimulated with an external source such as x rays or high-energy electrons, or nuclei undergoing radioactive decay, can emit radiation, which can reach the detector directly (the reference wave) or after scattering off the electrons of nearby atoms (the object wave). The pattern of interference between the direct and scattered radiation can be mapped out by varying the angular position of the detector. This pattern can be viewed as a hologram from which a real-space image can be reconstructed numerically.

Using this approach, Miklós Tegze and Gyula Faigel at the Research Institute for Solid-State Physics and Optics in Budapest, Hungary, reported the first x-ray hologram with atomic resolution five years ago[3] (see PHYSICS TODAY, May 1996, page 9). They used an external x-ray source to eject core electrons from strontium atoms in single-crystal $SrTiO_3$. As the atoms relaxed, they emitted fluorescent photons with a wavelength of 0.87 Å. Since photons were emitted not from a single Sr atom but from all the atoms in the crystal, the real-space image reconstructed from the hologram represented the average local environment around the Sr atoms. The amplitude of the holographic fringes was only about 0.3% of the background, but that was sufficient to allow the reconstruction of the 3D arrangement of the Sr atoms in the crystal.

A powerful extension of this technique of x-ray fluorescence holography (XFH) was demonstrated soon afterward by Thomas Gog and coworkers from the German Electron Synchrotron Laboratory (DESY), the University of California, Davis, and Lawrence Berkeley National Laboratory.[4] They switched the positions of the source and detector to obtain what's essentially the time-reversed process, sketched in figure 1b. Here, atoms within the sample served as detectors, and the strength of the fluorescence they emitted depended on the interference between the external radiation reaching them either directly (the reference wave) or after scattering off nearby atoms (the object waves). In this approach, the fluorescence detector was fixed and the incident direction of the source radiation was varied with respect to the crystal axes.

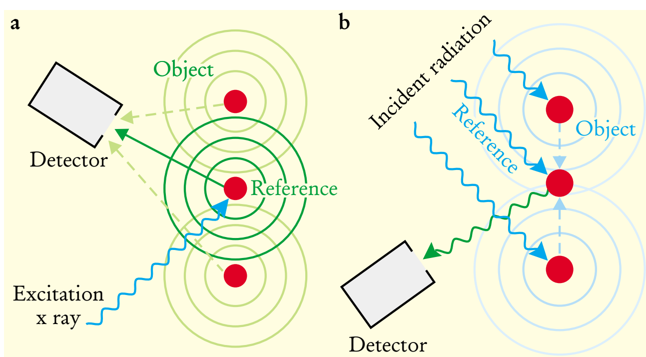

FIGURE 1. INTERNAL REFERENCE holography takes two forms. **(a)** In internal-source holography, incident radiation (blue) triggers an atom (red) to emit photons of a different energy (green). These photons can reach the detector either directly, forming the holographic reference wave, or after scattering off of other atoms, forming the object wave. Recording the interference as a function of angle around the sample produces a hologram. **(b)** Internal-detector holography is the inverse or time-reversed process. The radiation emitted by the detector atom depends on the total field it sees. Incident radiation (blue) can reach the detector atom either directly or after scattering off other atoms. Monitoring the emission of the detector atoms as the incident radiation direction is varied maps out the hologram. (Adapted from ref. 4.)

The twin problem

The time-reversed approach has the advantage of being able to record holograms at multiple energies above the x-ray absorption edge—hence the name multiple-energy x-ray holography (MEXH). John Barton (now with Hewlett-Packard) had previously shown that photoelectron holograms

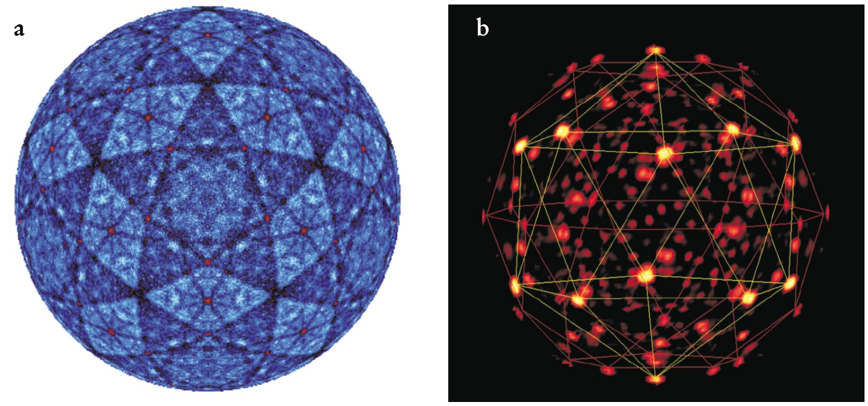

FIGURE 2. QUASICRYSTAL HOLOGRAM with x rays. A single-energy hologram **(a)** and reconstructed real-space image **(b)** around the Mn sites in the quasicrystal $Al_{70.4}Pd_{21}Mn_{8.6}$ clearly show the sample's icosahedral symmetry and the near-neighbor sites with the highest occupation probability, without having to appeal to a priori models. The reference Mn atom is at the origin in **(b)**, and the bright spots are a combination of the first coordination shell of Mn, the third of Al, and the fifth of Pd about the central Mn atom. (Adapted from ref. 7, courtesy of S. Marchesini.)

taken at multiple energies can be used in a Fourier-transform-like approach to remove so-called twin images and aberrations, ubiquitous problems for all holographic methods.[5]

Holography doesn't really record the phase of the object wave with respect to the reference wave, but only the cosine of the phase difference. A twofold sign ambiguity therefore remains. As a result, in the reconstruction of a 3D image from the hologram, one gets not only the real image but also a twin image that's inverted about the reference point (here, the fluorescing atom). The superposed images can be out of phase with each other, which can lead to cancellations, distortions, and problems with atom identification. But with holograms acquired at 8–10 different energies, one can solve the local structure unequivocally—something quite difficult to do with ordinary x-ray diffraction.

Demonstrations of the potential of x-ray holography are continuing. The scattering cross section for x rays scales with atomic number, and so heavy atoms are easier to see than light ones. However, last fall, Tegze, Faigel, and colleagues, working at the European Synchrotron Radiation Facility, achieved sufficient sensitivity with MEXH to image light atoms such as oxygen.[6] They have also recorded the local atomic structure in the icosahedral quasicrystal AlPdMn. Although it lacked long-range translational order, the quasicrystal had sufficient orientational order to allow the direct visualization of the icosahedral arrangement of atoms,[7] shown in figure 2, averaged over the handful of different Mn environments. Kouichi Hayashi and coworkers from Kyoto University and the Japan Synchrotron Research Institute have explored MEXH for imaging the local environment around zinc atoms doped into gallium arsenide.[8] And Larry Sorensen's group at the University of Washington has generated holograms with x rays produced by means of bremsstrahlung.[9]

γ-ray holography

"The biggest difficulty with all x-ray holography is that the contrast is very low," says Szöke. Nuclei with low-lying excited states can also serve as the radiation source for atomic-resolution holography.[2] Such nuclei, used for Mössbauer spectroscopy, can emit γ rays with very well-defined energy. These photons scatter not only off electrons, but also off nuclei through a resonant process that has a cross section two orders of magnitude larger. Consequently, γ rays can provide much better contrast, but only a few dozen isotopes have the requisite Mössbauer resonance to serve as reference nuclei and as scatterers.

Fortunately, the most popular Mössbauer isotope, iron-57, has a resonance at a wavelength of 0.86 Å, suitable for atomic-resolution holography. Using an epitaxial Fe film enriched in this isotope, Pawel Korecki at Jagiellonian University (now at DESY) and coworkers at the University of Mining and Metallurgy in Krakow, Poland, first demonstrated atomic-resolution holography with γ rays.[10] The γ rays were provided through the radioactive decay of cobalt-57. The researchers used the inverse, internal-detector configuration (figure 1b), thereby avoiding the need to embed ^{57}Co within the sample. The absorption of γ rays by ^{57}Fe, sensitive to the interference between direct and scattered radiation reaching the nuclei, was monitored through the flux of conversion electrons emitted as the nuclei relaxed.

Having the γ-ray source outside the sample has another advantage. As in Mössbauer spectroscopy, the frequency of the photons can be tweaked by adjusting the relative motion of the source with respect to the sample. In February, Korecki and colleagues capitalized on that ability to suppress twin images using "complex" holograms.[11] Working with the Mössbauer resonance essentially fixes the photon wavelength, but it's possible to change the photon phase. As with any resonance, the γ rays that scatter off the nuclei experience a phase shift that varies with the detuning from the center of the resonance. Using γ rays equally detuned on either side of the narrow Mössbauer resonance peak, the researchers could take linear combinations of two holograms to separate the real and imaginary parts. From the combination of those complex components, an accurate, twin-free real-space image can be reconstructed, as shown in figure 3.

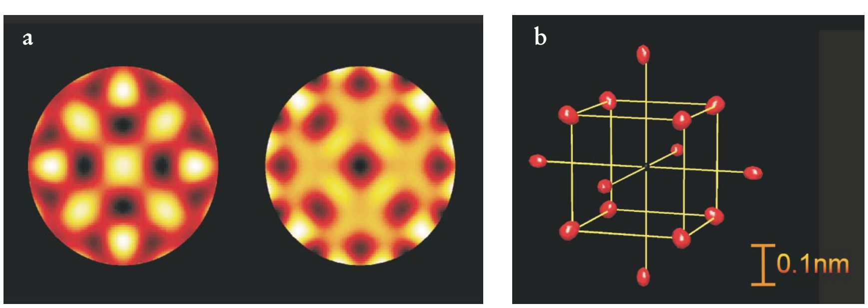

FIGURE 3. COMPLEX γ-RAY HOLOGRAPHY. (a) With γ rays on either side of a nuclear absorption peak, "real" (left) and "imaginary" (right) holograms—here of a film of iron-57—can be obtained in which the phases of the scattered object waves differ by $\pi/2$. **(b)** Combining these two holograms into a single, complex hologram allows this accurate reconstruction of the local real-space structure of the Fe crystal without distortion from twin images. The reference absorbing nucleus is at the origin. (Adapted from ref. 11, courtesy of P. Korecki.)

The exploitation of the γ-ray phase shifts near a resonance is similar to the x-ray crystallography technique of multiple-wavelength anomalous dispersion. When x rays close to absorption edges are used in diffraction, they also undergo phase shifts; by comparing diffraction patterns from x rays of different wavelengths, phase information normally lost in x-ray diffraction can be inferred, yielding additional insight into the underlying structure.

Work in progress

To a large extent, x-ray and γ-ray holography are currently detector-limited. But they place less stringent demands on the crystalline perfection of samples than standard x-ray diffraction does. "Whereas a 1° misalignment can kill normal x-ray diffraction," says Charles Fadley of UC Davis, "x-ray holography can tolerate many crystallites with a misalignment of up to a few degrees." Given the difficulty of crystallizing many materials, including biological and other large molecules, such samples may in the future be amenable to study by holographic methods even though they aren't candidates for diffraction investigation.

Because the Mössbauer resonance can be shifted due to hyperfine coupling to electrons, γ-ray holography has the potential for imaging the local magnetic environment. It may also find use in imaging low-dimensional systems. RICHARD FITZGERALD

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