Development of a new holographic method with resonant X-ray scattering

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Abstract

Complex X-ray holography (CXH) using resonant scattering is proposed as a new atomic resolution holography method. CXH provides us a solution for the twin-image problem as well as elemental identification in real space. Accurate differences among intensities recorded at several X-ray energies around an absorption edge must be experimentally obtained in the CXH method. Taking into account that the holographic signal is of the order of 0.1% of its background, we find it difficult to carry out using ordinary technique for hologram measurement. Thus, in order to measure holograms with a very good S/N ratio, a sample was cooled about 100 K and fluorescent X-rays were focused on a detector with a cylindrical graphite analyzer in the X-ray fluorescence holography apparatus at SPring-8. Ga fluorescent holograms of GaAs were recorded at energies near the As K absorption edge. A change of holographic oscillations due to the resonant scattering, which is expected from the computer simulation, was firstly observed.

Keywords: X-ray fluorescence holography; Local structure; GaAs

1. Introduction

In 1986, Szöke [1] proposed atomic resolution holography using fluorescent X-rays and photoelectrons as a reference wave. The hologram directly provides us a 3D image of atomic configurations by a simple numerical algorithm [2]. This idea was first realized with photoelectrons in 1990 [3]. Holography with fluorescent X-rays, i.e. X-ray fluorescence holography (XFH), was performed by Tegze and Faigel [4] in 1996. Subsequently, its basic researches [5,6] and application to dopants [7], a quasi crystal [8], a FePt film [9,10], and a SiGe semiconductor [11] were reported.

One of serious problems of XFH is a twin image that appears in an image reconstructed from holograms. The conjugate image often overlaps with the real image. This causes a distortion of atomic images [12]. The twin-image problem results from the fact that observable fluorescent intensities include only the real part of the complex interference terms. In order to solve this problem, two ideas have been proposed, i.e. the multiple energy X-ray holography (MEXH) [13] and the two energy method [14].

In MEXH, image functions reconstructed at various energies are summed by Barton’s multiple-energy algorithm [15]. In the summed-up image, phases are constructively added at true atomic positions, while they are randomly added at twin image positions. In order to eliminate the conjugate image, 5–10 hologram patterns must be recorded in this method. This is quite time-consuming. Nishino et al. [14] proposed a new method that requires only two holograms observed at two energies about 300 eV apart. In its reconstructive algorithm, the phase of the conjugate image is locked and is canceled by calculating a difference of the two images.

Recently, Omori et al. [16] have proposed resonant X-ray fluorescence holography (RXFH) which enables us to reconstruct an atomic image with element selectivity using differential holograms near an X-ray absorption edge. RXFH uses the same algorithm as MEXH. A large change of a scattering factor due to a resonant effect is, however, observed only within about 200 eV around the absorption edge. Taking into account that the multiple-energy algorithm is effective for several holograms recorded in the range of more than 4 keV [10], the twin-image problem is hardly solved by RXFH [17]. Thus, we proposed complex X-ray holography (CXH) [18] using resonant X-ray scattering, which is based on the idea of complex...
γ-ray holography [19]. In this article, we explain the theory of CXH and the experimental technique for obtaining accurate hologram data necessary to CXH. Finally, measured data are discussed by comparing with that calculated.

2. Principle of complex X-ray holography

XFH has two measurement methods, i.e., internal source holography (ISH) [4] and internal detector holography (IDH) [16], as explained in Fig. 1(a) and (b), respectively. In ISH, a wave source is an atom of a specific element in a sample emitting fluorescent X-rays. A part of fluorescence is scattered by neighboring atoms and interferes with the radiations directly traveling outside the sample. This interference forms a hologram with atomic resolution. On the other hand, in IDH, which is based on the optical reciprocity of ISH, a hologram is formed by interference at fluorescent atoms between incident X-rays and those scattered by neighboring atoms. The hologram is recorded by changing the direction of the incident X-rays. Advantage of IDH is that any energy above an absorption edge can be chosen for recording holograms. The CXH is carried out by this IDH method.

In IDH, normalized holographic intensities are given by

$$\chi(k) = r_c \sum_j \frac{f_j}{a_j} e^{i(ka_j - qa_j)} + c.c.,$$  

where $r_c$ is the classical electron radius, $k$ the wave number vector of incident X-rays, $a_j$ the distance between a fluorescent atom (emitter) and $j$-th scattering atoms (scatterer), and $c.c.$ the complex conjugate of the first term. Here, we consider the anomalous dispersion term of the X-ray scattering factor. The overall scattering factor is $f_j = f_{j0} + if_{j1}$, where $f_{j0}$ is the atomic form factor, and $f_{j1}$ and $f_{j1}$ are the real and imaginary parts of the anomalous dispersion term, respectively. The holographic intensities of Eq. (1) can be rewritten in the form of

$$\chi(k) = 2r_c \sum_j \frac{(f_{j0} + f_{j1})\cos(\varphi_{k,a_j}) - f_{j1}\sin(\varphi_{k,a_j})}{a_j},$$

where $\varphi_{k,a_j}$ is the phase difference between the incident X-rays and the scattered ones.

Let us assume a binary compound crystal consisting of elements X and Y and the K absorption edge of Y is the higher-energy side than that of X. Holograms of X K fluorescence using the resonant scattering of Y atoms are calculated. Incident X-ray energies $E^A$, $E^B$, and $E^C$ close to the Y K absorption edge are selected, as they are depicted in Fig. 2. X-ray scattering factors of the Y element at these three energies are $f^A = f^A_0 + f^A_1 + if^A_1$, $f^B = f^B_0 + f^B_1 + if^B_1$, and $f^C = f^C_0 + f^C_1 + if^C_1$ where $f^A_0 = f^B_0 = f^C_0 = f_0$, $E^A$ and $E^B$ are selected just above and below the absorption edge so as to equalize $f^A_1$ with $f^B_1$. $E^A$ and $E^C$ are about 100 eV apart so that $f^A_1$ is nearly equal to $f^A_1$, and the difference is below 1% of $(f^C_1 - f^B_1)$ in any element from Al to Pb. In addition, a change of the X-ray scattering factor of X is negligible near the absorption edge of Y. Thus, differential holograms of $\chi^B - \chi^A$ and $\chi^C - \chi^B$...
are expected as
\begin{equation}
\chi^B(k_B) - \chi^A(k_A)
= 2r_c \sum_j \left( f_j^B - f_j^A \right) \cos(\varphi_{k_A}) - (f_j^B - f_j^A) \sin(\varphi_{k_B}) \tag{3}
\end{equation}
\begin{equation}
= 2r_c \left( f_j^A - f_j^B \right) \sum_j \frac{\sin(\varphi_{k_A})}{a_j} \tag{4}
\end{equation}
and
\begin{equation}
\chi^C(k_C) = \chi^B(k_B)
= 2r_c \sum_j \left( f_j^C - f_j^B \right) \cos(\varphi_{k_B}) - (f_j^C - f_j^B) \sin(\varphi_{k_B}) \tag{5}
\end{equation}
\begin{equation}
= 2r_c \left( f_j^C - f_j^B \right) \sum_j \frac{\cos(\varphi_{k_B})}{a_j}, \tag{6}
\end{equation}
where \( \mathbf{k} = \mathbf{k}_A + \mathbf{k}_B + \mathbf{k}_C \).

The differential holograms in Eqs. (4) and (6) in electron units are redefined as they are shown below.
\begin{equation}
\Delta \chi_f(k) = \frac{\chi^B(k_B) - \chi^A(k_A)}{f_j^A - f_j^B} = 2r_c \sum_j \frac{\sin(\varphi_{k_A})}{a_j} \tag{7}
\end{equation}
and
\begin{equation}
\Delta \chi_l(k) = \frac{\chi^C(k_C) - \chi^B(k_B)}{f_j^C - f_j^B} = 2r_c \sum_j \frac{\cos(\varphi_{k_B})}{a_j}. \tag{8}
\end{equation}

The \( \Delta \chi_f(k) \) and \( \Delta \chi_l(k) \) correspond to real and imaginary holograms recorded at \( \mathbf{k} \). A complex holographic function \( \chi_{\text{complex}}(k) \) is expressed by
\begin{equation}
\chi_{\text{complex}}(k) = \Delta \chi_f(k) + i \Delta \chi_l(k). \tag{9}
\end{equation}
The real space function is obtained by Barton’s single-energy algorithm [2] of
\begin{equation}
U_k(r) = \int e^{-ikr} \left( \Delta \chi_f(k) + i \Delta \chi_l(k) \right) d\Omega. \tag{10}
\end{equation}
The \( U_k(r) \) is a complex value, and its absolute \(|U_k(r)|\) is used as the atomic image and exhibits only Y atoms without the twin image.

### 3. Technical improvement

CXH finds it difficult to experimentally carry out, since the signal of the complex hologram is of the order of 0.01% of isotropic fluorescent radiations. Incidentally, it is about one-tenth of the ordinary fluorescent hologram. Therefore, holograms were measured with the statistical accuracy within 0.01% using the following XFH apparatus at SPring-8 [20] schematically shown in Fig. 3.

The sample was set on the two \( \theta \)- and \( \phi \)-axis rotation stages, where \( \theta \) is an angle between the incident beam and the surface normal, and \( \phi \) is an azimuthal angle around the surface normal. The sample was cooled at about 100 K with a \( \text{N}_2 \) gas cryostream (Oxford Co.). This suppresses thermal vibrations of atoms to increase holographic signal about 10 ~ 30% of that at room temperature. The sample was mounted on the alumina-ceramics rod in Fig. 4 to reduce heat conduction. In addition, in order to prevent to frost, it is placed in the small chamber with an X-ray window of 7.5 \( \mu \text{m} \) thick polyimide film. A singly bent graphite single crystal [21] with a 25-mm radius (Matsushita Electric Co.) in Fig. 4(b) was adopted as an analyzer. The four graphite crystals were placed to form a cylindrical shape to focus fluorescent X-rays on the detector. In the center of this analyzer, a direct-beam stopper was set.
4. Experimental detail

This new measurement system was tested at the undulator beam line BL37XU in SPring-8. GaAs(110) single-crystal plate (5 × 5 × 0.35 mm³) was selected as the sample. GaAs has the zinc-blende structure with a lattice parameter of 5.65 Å [22]. Temperature parameter \( B \) of GaAs at 100, 300 K are 0.2, 0.5, respectively [23]. The incident beam was monochromatized using a Si(111) double-crystal monochromator, and a Rh coated mirror was used to suppress higher harmonic X-rays. In this measurement, the pure IDH scheme [24] was adopted for collecting hologram patterns. In the scheme, the detector was set on the normal axis to the sample surface, as shown in Fig. 3. The beam size at the sample was adjusted to be 0.3 mm along the horizontal direction and 0.5 mm along the vertical direction. The incident beam intensity was monitored by detecting X-rays scattered from a polyimide film of 125 \( \mu \)m thickness using a Si PIN photodiode. Incident X-ray energies were selected to 11767 and 11862 eV, which were 100 and 5 eV below As \( K \) absorption edge (11867 eV), respectively, since contribution of the secondary excitation and XAFS oscillations [18] make analyses more complicated above an absorption edge. Ga \( K_a \) fluorescence emitted from GaAs was analyzed and focused on another Si PIN photodiode. The currents in the Si PIN photodiode were amplified by 10⁷ V/A, was converted from a voltage to a frequency, and collected by a scaler. Intensities of Ga \( K_a \) fluorescence were measured as a function of \( \phi (0^\circ \leq \phi \leq 360^\circ) \) at \( \theta = 35^\circ \). The dwelling time for each point was 0.1 s and the increments of angles were set 0.1°. The total intensity of Ga \( K_a \) fluorescence at each point was about 10⁷ counts. It took about 600 s to collect the present data at a single incident energy.

5. Results and discussion

Fig. 5 shows the normalized holographic oscillation at 11767 eV. Sharp peaks due to X-ray standing wave (XSW) reflect the mirror symmetry in GaAs(110). In order to improve the statistical accuracy, symmetrically equivalent data were averaged, referring to these XSW peaks. For a further analysis, Gaussian high and low frequency-pass filters [25] with \( \sigma = 3.0k \) and \( \sigma = 0.05k \), respectively, were applied. The \( \sigma \) is a variable parameter which smoothes the original data and the \( k \) is the wave number of incident X-rays. Filtered oscillations include only environmental structural information around Ga. It reproduced with 0.01% accuracy.

Figs. 6(a) and (b), respectively, show the experimental and numerically simulated holographic oscillations at two energies. This simulation was carried out in a GaAs cluster with a radius of 50 Å containing 23157 neighboring atoms around Ga at the center. These holographic oscillations were calculated by a single-scattering cluster model [26], and moreover, the same filtering processes as experimental analysis were applied. Anomalous dispersion terms of As and Ga at these two energies are summarized in Table 1. These values were quoted from the table [27] calculated by...
Cromer and Liberman’s method [28,29]. In the present energy region, the difference of holographic oscillations is due to the difference of $f'$ of As, since $f'$ and $f''$ values of Ga and $f''$ of As are almost constant. The fine shapes and absolute values of the experimental and calculated profiles are different. This is mainly due to the size of cluster used in the computer simulation. The maximum size of cluster we can calculate in reasonable time is a radius of 50 Å which is too small to express the real crystal. Therefore, this simulation does not completely reproduce the present experiment. However, tendency of the experimental profile in 11.767 eV roughly agree with that of simulation and especially magnitude relation of two-energy profiles roughly equal at angles indicated by arrows. Thus, in the present measurement at the As K absorption edge, we may say that the difference between the two profiles due to the anomalous dispersion term of As is roughly recorded.

6. Conclusion

We proposed the CXH method which solves the twin-image problem and has element identification. A signal of a complex hologram is very small, i.e. the order of 0.01% of isotropic fluorescent radiations, while the ordinary fluorescent hologram is of the order of 0.1%. In actual experiment, therefore, holograms must be measured within 0.01% accuracy. A new system, where a sample was cooled at about 100 K by a cryostream and a fluorescent X-rays were focused on a detector by a cylindrical graphite analyzer, was installed in the XFH apparatus at SPring-8. Ga fluorescent holograms were measured in GaAs at the two energies below As K absorption edge using this system. Although the shape and amplitude between experimental and simulated profiles were quite different, the magnitude relation of these profiles equaled at some angles. We think that this is due to the anomalous X-ray scattering and positively promise clearer 3D atomic image without any experimental errors such as the twin image. In near future, the CXH method will realize a structure analysis including a complete phase.

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Table 1

| Energy (eV) | $f'$ of As | $f'$ of Ga | $f''$ of As | $f''$ of Ga |
|------------|-----------|-----------|-----------|-----------|
| 11.767     | $-4.369$  | $-1.138$  | $0.504$   | $3.112$   |
| 11.862     | $-7.581$  | $-1.067$  | $0.503$   | $3.072$   |
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