Recent Advances in X-Ray Fluorescence Holography*

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X-ray fluorescence holography (XFH) provides three dimensional atomic images around specified elements. The XFH uses atoms as a wave source or monitor of interference field within a crystal sample, and therefore it can record both intensity and phase of scattered X-rays. In this article, I show the theory including solutions for twin image problem, advanced measuring system, applications to dopants in silicon steel and shape-memory alloy related material, a new holographic method with X-ray excited optical luminescence. [DOI: 10.1380/ejssnt.2011.363]

Keywords: X-ray fluorescence holography; X-ray holography; X-ray scattering; single crystal; impurity

I. INTRODUCTION

For developments of state-of-art materials, structure analyses with atomistic order are necessary. Therefore, electron microscopes and scanning prove microscopes have been widely used in the scientific and industrial fields. X-ray analyses, such as X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS), are also useful for this purpose. However, since they require adequate structure models and data-fitting procedures, determinations of atomic arrangements are not straightforward unlike electron microscopes and scanning prove microscopes. On the other hand, atomic resolution holography with X-ray, electron and neutron provides 3D atomic images around specific elements by a simple Fourier transformation.

X-ray fluorescence holography (XFH) is one of the atomic resolution holography methods, and it uses X-ray fluorescence to record the atomic arrangements around the fluorescing atoms. In 1986, Szőke pointed out that fluorescent X-rays and photoelectrons from ionized atoms in a single crystal formed atom-resolved holograms [1]. Although the photoelectron holography was realized in 1990 [2], only a feasibility study of the XFH by a computer simulation started at that time [3]. The reason for this is the weakness of the holographic oscillation of 0.1-0.01% in the angular distribution of X-ray fluorescence intensity. An XFH experiment was first performed by Tegze and Faigel in 1996 as a demonstration of the structural analysis of strontium titanate (SrTiO₃) [4]. They measured the spherically distributed fluorescence intensity varying the detector position. However, since this method can record the holograms only at X-ray emission lines, such as Kα and Kβ, Gog and his coworkers proposed and demonstrated the inverse XFH method, which records holograms with waves of incident X-rays [5]. In inverse XFH, a holographic pattern can be obtained by detecting the fluorescence by varying the sample orientation relative to the incident beam. If one used an energy tunable synchrotron radiation source to the inverse XFH, very high quality atomic images can be obtained owing to holograms recorded multiply at different energies (wavelengths).

First XFH measurement by Tegze and Faigel required a few months using laboratory X-ray source due to the very weak signals. Nowadays, the XFH can measure one hologram within a few hours by a combination a strong synchrotron radiation source and a fast X-ray detector [6]. The multiple energy hologram offers a high-quality atomic image with 0.5 Å spatial resolution, in which ghost images are highly suppressed [7]. Recent technical advances provide a data set with extremely high statistical accuracy, and can display light atoms such as oxygen [8] and a specific element atoms using resonant X-ray scatterings [9]. Moreover, the reconstructible volume has widened up to few nm in a radius. This feature makes us possible to analyze middle-range local structure, which offers more information than the short range local structure obtained by XAFS. Since the sample of XFH needs a regular orientation of atomic arrangement around a specific element, the amorphous or powder samples cannot be measured. However, it is not limited to systems with a long-range order but can also be applied to cluster, surface adsorbates, quasicrystal [10] and impurities [11]. In addition to these, recently, our XFH group has shown the strong point of the middle range local structure by revealing lattice distortions in mixed crystals [12, 13] and phase transition materials [14, 15].

In the present review, I show the theory of the XFH in two modes, advanced measuring system, data processing for reconstruction of the atomic images, applications of

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FIG. 1: Principle of XFH. (a): normal mode. (b): inverse mode.
dopant and phase transition and X-ray holography using X-ray excited optical luminescence (XEOL).

II. THEORY

XFH has normal and inverse modes as mentioned in the preceding section. Figure 1 shows the principles of these two modes using dimers. As explained in Fig. 1(a), in the normal mode, atom A is excited by X-ray or electron and emit a fluorescent X-ray. Then, a part of the fluorescent X-ray wave is scattered by a neighboring atom B. Here, the scattered and nonscattered fluorescent photons play roles of the objective and reference waves in holography. An interference of these two waves produces an intensity modulation on a spherical surface surrounding the sample. Actually, the hologram is measured as an intensity distribution of the X-ray fluorescence far from the sample. In this case, the path difference between these reference and object waves AB-AC is expressed as \(d(1 - \cos \theta)\), where \(d\) is the interatomic distance A and B and \(\theta\) is the angle of BAC in Fig. 1. The X-ray phase is shifted by \(\pi\) due to the negative charge of the electron when scattering by atoms. Thus, phases of the reference and object waves coincide and an intensity maximum appears when \(d(1 - \cos \theta)\lambda\) is equal to a half-integer, where \(\lambda\) is the wavelength of the fluorescent X-ray. Using the atomic structure factor of atom A, \(f(\theta, \lambda)\), for X-ray at \(\lambda\), the relative intensity of fluorescence \(I(\theta, \lambda)\) can be expressed by

\[
I(\theta, \lambda) = \left[ 1 - \frac{\lambda r_e f(\theta, \lambda)}{2\pi d} e^{i2\pi d(\cos \theta - 1)/\lambda} \right]^2 = 1 - 2 Re \left( \frac{\lambda r_e f(\theta, \lambda)}{2\pi d} e^{i2\pi d(\cos \theta - 1)/\lambda} \right) + \frac{\lambda r_e f(\theta, \lambda)}{2\pi d} e^{i2\pi d(\cos \theta - 1)/\lambda} \right]^2, \tag{1}
\]

where \(r_e\) is the classical electron radius. Since a scattering cross section of the atom for the X-ray is extremely small, the volume of \(\lambda f(\theta)/2\pi d\) is less than \(10^{-3}\). Therefore, Eq. (1) can be approximated as

\[
I(\theta, \lambda) \simeq 1 - 2 Re \left( \frac{\lambda r_e f(\theta, \lambda)}{2\pi d} e^{i2\pi d(\cos \theta - 1)/\lambda} \right). \tag{2}
\]

The second term refers to the hologram formed by atom B.

The inverse mode was proposed based on the idea of the optical reciprocity of the normal mode. Figure 1(b) shows the principle of the inverse mode. In this case, an incident X-ray wave directly coming to atom A (reference wave) is interfered with a wave scattered by atom B (object wave), which forms X-ray standing wave field around atom A. This pattern varies by the direction of the incident X-ray beam, and this causes the intensity variation of the fluorescent X-ray from atom A as a function of the incident beam direction, which is equivalent to the hologram in the normal mode. The normalized intensity of the fluorescence can be expressed by Eq. (2). Here, \(\lambda\) is the wavelength of the incident X-ray. Since the inverse XFH allows holograms to be recorded at any incident energy above the absorption edge of an emitter, the twin image effect is suppressed and the spatial resolution of an atomic image is improved.

III. HOLOGRAM CALCULATIONS USING DIMER AND LARGE CLUSTER

I calculated a hologram using a Cu-I dimer to check how the hologram pattern appear. Here, Cu and I atoms act as emitter (atom A in Fig. 1) and scatterer (atom B in Fig. 1), respectively. Figure 2(a) shows the calculated hologram with 27.8 keV incident X-rays in inverse mode. The pattern is displayed in \(k\)-space, where \(k_x = |k| \cos \phi \cos \theta\) and \(k_y = |k| \sin \phi \cos \theta\). The \(k(=2\pi/\lambda)\) is the wave number vector of the incident X-rays. (In normal mode, the \(k\) is the wave number vector of the fluorescent X-rays.) The hologram shows simple stripe pattern.

Next, I calculated a hologram using a more realistic cluster model. Here, Eq. (2) is changed to a more general formulation of the generating hologram:

\[
I(k) \simeq 1 - 2 Re \sum_j \left[ \frac{r_\epsilon f_j(\theta_{\epsilon j})}{r_j} e^{i(-k \cdot r_j - kr_j)} \right] + \sum_j \frac{r_\epsilon f_j(\theta_{\epsilon j})}{r_j} e^{i(-k \cdot r_j - kr_j)} \right]^2, \tag{3}
\]

where \(\theta_{\epsilon j}\) is the angle between \(k\) and \(r_j\). Although Eq. (3) is used for the inverse mode, the \(k\) should be replaced by the \(-k\) in the normal mode. The second term indicates the holographic amplitude, whose value is \(\sim 10^{-3}\). The value of the third term is \(\sim 10^{-6}\) except under Bragg condition. Here, we calculated 33453 atoms CuI cluster with zinc blend structure, whose radius is 60 Å. The incident X-ray energy was 27.8 keV, and the emitter atom was Cu. The obtained hologram pattern shows fine structure due to the interference by far atoms. Line structures in the
IV. RECONSTRUCTION OF ATOMIC IMAGE

Holography, which we always see in our lives, is Fresnel holography. In the Fresnel holography, real space image can be seen by irradiating laser light on a film recording a hologram. XFH cannot provide real space images using such a method, but they can be obtained by applying a Fourier-transformation like algorithm to the hologram using a computer. At the reconstruction, Helmholtz-Kirchhoff formulae is used [16];

\[ U(r) = \int \int e^{-kr} \chi(k) d\sigma. \]  

Using Eq. (4), (110) plane of CuI was reconstructed from the hologram in Fig. 2 (b). Figure 3(a) is the resulted atomic image. Solid and dashed circles in the figure indicate theoretical positions of I and Cu atoms. Background intensity in the reconstruction is high as a whole. Therefore, although first neighbor In atoms are visible, other atomic images are hidden by the background. The reconstruction is center symmetric, and therefore, the atomic images also appear at the position center-symmetric to the first neighbor In atoms. These atomic images are called “conjugated images”. In addition to this, many artifacts are created in the reconstruction.

These problems can be suppressed by the multiple energy reconstruction, which was proposed by Barton [17]. The Barton algorithm can be expressed by

\[ U(r) = e^{ikr} \int \int e^{-kr} \chi(k) d\sigma. \]  

This equation is known to be a modification of Eq. (4). The real space image is obtained by Eq. (4) as complex values. But normally the image is displayed as absolute values like Fig. 3. However, the phases of the true and its conjugated images are different. Barton focused this character. Using Eq. (5), the phase of the true images are constant even when the X-ray energies are different. In contrast, the phase of the conjugated images are not constant. Thus, the conjugated image can be diminished by summation of the reconstructions from holograms at different X-ray energies. I again calculated holograms at
26.8, 27.3, 27.8, 28.3 and 28.8 keV with CuI cluster in Fig. 2(b), and reconstructed atomic images as shown in Fig. 3(b). The conjugated image is perfectly removed, and artifacts are suppressed. Compared to the atomic images by single energy hologram in Fig. 3(a), the atomic images by multiple energies are largely improved.

V. EXPERIMENTAL SETUP

As explained in previous session, XFH has two modes: normal and inverse modes. The holography experiments in normal and inverse modes can be carried out using the setup in Fig. 4 (a). The samples must have translational symmetry of atomic arrangements over a few nm. This condition is satisfied in single crystals and epitaxial films. Moreover, to suppress the sample shape effect, usually the surfaces of the samples are polished to be flat. In the normal mode experiment, the incident angle $\theta_1$ is fixed, and the azimuthal angle $\phi$ and the X-ray exit angle $\theta_2$ are scanned two-dimensionally. Normally, the steps of $\phi$ and $\theta_1$ are less than 1°. Slits for limiting these angles are set in front of the detector. To record holograms largely in $k$-space, angular ranges of $\phi$ and $\theta_2$ ($0^\circ \leq \phi \leq 360^\circ$, $0^\circ \leq \theta_2 \leq 80^\circ$) should be large as much as possible.

In the inverse mode, the role of $\theta_1$ is replaced by that of $\theta_2$ in the normal mode. Therefore, the $\theta_2$ is fixed, and the intensity variation of the X-ray fluorescence as function of the $\phi$ and $\theta_2$ becomes a hologram equivalent to one in the normal mode. Ideally, the inverse XFH should detect all fluorescence photons from the sample during the measurement. However, this is not realistic. Thus, it desires to collect the fluorescence photon as much as possible, and this smears out the component of the hologram in normal mode. The holography experiments in synchrotron radiation facilities take an advantage of energy-tunable X-ray sources. However, a beam time is limited to a few days, and thus, the solid state detector with a few thousand cps are not adequate. For this reason, photons of wanted fluorescence line must be detected at a very high count rate. Avalanche photodiode is a typical fast X-ray detector, and its maximum count rate is $10^8$ cps. However, because of its poor-energy resolution, the X-ray fluorescence must be analyzed and focused with a cylindrical or toroidal crystal analyzer [18], as shown in Fig. 4(b). By using such a system, one hologram can be measured within a few hours. The solid angle acceptance of the toroidal analyzer is around ten times larger than that of the cylindrical analyzer although the analyzed fluorescence line is limited to be one.

VI. APPLICATIONS

A. Copper in silicon steel

Structural analyses of environments around dopants in single crystals are one of important applications of the XFH. In this section, I introduce our study of local structure around Cu in a silicon steel. Silicon steels contain about 6% silicon, and show high magnetic permeability. Thus, the silicon steels are practically important types of electrical steel for application in transformers, motors and generators. The concentration of Cu is 0.073 at.%. Although other impurities were also included in the silicon steel, the Cu and Mn play an important role of the crystal growth. Therefore, we focused the Cu and tried to reconstruct its environment. The XFH experiment was carried out at BL47XU in synchrotron radiation facility SPring-8. The incident energies were 19.0-22.0 keV with 0.25 keV steps. These X-rays excited an extremely strong Fe K fluorescence from the sample. This was mostly eliminated using a toroidal graphite analyzer for Cu Kα line. The toroidal graphite analyzer focused only Cu Kα fluorescent X-rays on the avalanche photodiode. The average count rate of the avalanche photodiode is two million cps. The holograms were recorded by measuring two-dimensional angular variation of the Cu Kα intensity.

We could successfully obtain 13 holograms with enough...
statistic accuracy, despite the very low concentration of the Cu. Figure 5 shows the hologram taken at 18.0 keV. X-ray standing wave lines were clearly visible. Using these data, 3D atomic images were reconstructed. Figure 6 shows Fe atomic arrangement with bcc structure, and Fig. 7 shows atomic images at typical five planes. Circles in Fig. 7 indicate theoretical positions of bcc Fe, and the reconstructed atomic images well agree with these. Consequently, it is known that most of Cu atoms were substituted for Fe atoms. At plane E far from the origin, the all atomic images can be seen clearly. This fact revealed that XFH makes us possible to elucidate not only short range order structure but also middle range order structure.

B. Shape memory alloy related material

Ti$_{50}$Ni$_{44}$Fe$_6$ is a shape memory alloy related material of TiNi series. The shape recovery phenomena of the alloys is caused by martensitic phase transition. But, the martensitic phase transition is suppressed in TiNi alloy including over 6% Fe. Instead the Ti$_{50}$Ni$_{44}$Fe$_6$ shows the phase transition, parent (P) phase – incommensurate (IC) phase – commensurate (C) phase, on cooling. The C-phase has been regarded as a precursor of the martensitic phase transition. Therefore, it is believed that the study of the C-phase would reveal the mechanism of the martensitic phase transition.

The XFH experiment was carried out at BL-6C in synchrotron radiation facility, Photon Factory, KEK. The incident energies were 8.0-12.0 keV with 0.5 keV steps. The toroidal graphite analyzer was used for collecting the Fe Kα fluorescent X-rays. The average count rate of the avalanche photodiode is two million cps. The sample temperatures were controlled at 100 K and 225 K, which correspond to P- and C-phases, respectively, by a N$_2$ gas spraying cooler. Figures 8(a) and (b) show atomic images of Ni/Fe plane in P- and C-phases, respectively. In general, the atomic image intensity decreases with the increase of the distance from the origin. Of course, such a trend is observed in both images. However, its details of P- and C-phases are different. That is to say, intensities of near atoms, such as 110, 200 and 210, in C-phase are stronger than those in P-phase. In contrast, intensities of far atoms, such as 300, 310 and 320, in C-phase are weaker than those in P-phase. To display the intensity changes of the atomic images by the phase transition, ratios of the image intensities at z = 0.0 and 3.0 Å, where Ni and Fe exist, are shown as contrasts of circles in Fig. 9. Since the atomic images within a radius of 8 Å are enhanced by the phase transition, rigid cluster-like structures with a radius of 8 Å were formed at C-phase.

Figures 8(c) and (d) shows Ti atomic images at z = 1.5 Å in P- and C-phases, respectively. Compared both the figures, it is found that the intensities of first neighbor atoms strongly increased by the phase transition. The ratio of the image intensities at C- and P-phases is 2.2. This intensity change is related to the fluctuation of neighboring Ti atom. To confirm this, X-ray absorption fine structure (XAFS) measurement was carried out for the same Ti$_{50}$Ni$_{44}$Fe$_6$ sample at P- and C-phases. However, the fluctuations of first neighbor Ti atoms along a radial direction for two phases are too small to explain this intensity change. Therefore, it is considered that the atomic fluctuation along angular direction at P-phase was much larger than that at C-phase. Actually, we calculated the mean square displacements of the neighboring Ti atom along angular direction from the image intensities. The estimated values at P- and C-phases are less than 0.1 Å.
FIG. 8: Atomic images on the (001) lattice plane at $z = 0$ Å (upper) and $z = 1.5$ Å (lower) in the $P$ (left) and $C$ phases (right). The intersections of the dotted lines indicate the ideal positions of the Ni/Fe atoms in (a) and (b) and the Ti atoms in (c) and (d). Taken from Ref. [14].

FIG. 9: Atomic arrangements of Ni/Fe planes with intensity ratios of $C$ and $P$ phases at (a) $z = 0$ Å and (b) $z = 3.0$ Å. The dashed circles with the radius of 8 Å indicate the area of a clusterlike structure in the $C$ phase at 100 K. The gray bar indicates the intensity ratios of the $C$ and $P$ phases. The lightness shows the atomic image enhancement due to phase transition to $C$ phase. Taken from Ref. [14].

and more than 0.4 Å, respectively. The neighboring Ti atoms were strongly stabilized after phase transition to $C$-phase. The dopant Fe atoms cause the positions of the first Ti atoms to fluctuate in the $P$-phase. This distortion plays an important role in maintaining the uniform atomic arrangement of Ti$_{50}$Ni$_{42}$Fe$_6$. On the other hand, because of the suppression of the fluctuation in the $C$-phase, the atoms in the clusterlike structures are self-organized in their positions and become locally stable. Since such clusters are not suitable for forming an entire crystal, the atoms between the clusters may disorder to bridge the clusters, and thus the image intensities of the
In the case of Al, the luminescence intensity is proportional to the product $y(\text{Å})$ of Al. And, if the sample incident X-rays are considered to be different from those the incident X-rays. Thus, the atoms absorbed the in-nescence is mostly excited by secondary radiations, such as low compared to that of the X-ray fluorescence, the lumi-
escence while the sample orientation is changed. However, since excitation energy of the luminescence was extremely high compared to that of the X-ray fluorescence, the lumi-
escence is sensitive to the chemical state of the mate-
rial. XAFS measurement with XEOL can measure a site-
selective X-ray absorption spectrum. In general, XAFS measurement is performed by detections of transmitted X-rays or fluorescent X-rays. And, such an analogy can be applied to the measurement of the atomic resolution hologram in inverse mode. Here, we can understand the X-ray holography with XEOL by replacing the X-ray fluorescence. Therefore, we can record the atomic resolution hologram by mea-
suring two-dimensional intensity variation of the lumines-
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cence is mostly excited by secondary radiations, such as secondary, Auger and photo electrons, rather than by the incident X-rays. Thus, the atoms absorbed the in-
cident X-rays are considered to be different from those emitted the luminescence, unlike X-ray fluorescence. In X-ray holography with XEOL, all atoms absorbed X-rays play a role of atom A in Fig. 1(b). And, if the sample includes several elements, contribution of each element to the luminescence intensity is proportional to the product of its X-ray absorption coefficient and its concentration. In the case of $\text{Al}_2\text{O}_3$, contribution of the Al is 30 times larger than that of O. Thus, the hologram measurement of $\text{Al}_2\text{O}_3$ with XEOL provides 3D atomic image around Al.

Here, we used $\text{Al}_2\text{O}_3$ as the sample. The holography experiment was carried out at BL37XU in SPring-8. The emitted luminescence from the $\text{Al}_2\text{O}_3$ [19] was detected by a photon counter. The energy of the incident X-rays was 15.0 keV. Figure 10 shows the measured hologram pattern. Although we tried to reconstruct the real space image from the hologram by Barton reconstruction algo-
rithm, clear atomic images could not be seen due to the single energy hologram. To overcome this difficulty, we used a scattering pattern extraction algorithm using the maximum-entropy method (SPEA-MEM) [20], which is proposed by Matsushita et al. Figures 11(a) and (b) show the obtained real space images for (0001) plane at $z = 0.0$ and 1.1 Å, in which Al and O atoms exist, respectively. Al occupies two distinct sites in the (0001) plane, and therefore, two types of environments are overlapped in Fig. 11. From the resulting atomic images, neighbor Al atoms indicated by A, B and C are successfully reconstructed, al-
though the image of atom B shifts toward the origin. In addition, oxygen atoms seem to be reconstructed despite the smallness of their scattering cross sections. The rings formed by the connections among the neighbor atoms indicated by D, E, F and their equivalents are certainly observed in Fig. 11(a). However, the real-space image on the O plane is generally blurrier than that on the Al plane, because of the complex atomic arrangement and small X-ray scattering cross section of The Al atom.

The holography measurement using X-ray fluorescence is generally difficult for light elements, such as Al or Si, because of the absorption of their fluorescence by air. Our results demonstrate that hard X-ray holography measure-
ment is possible for light elements using XEOL [21].

C. X-ray holography using X-ray excited optical luminescence

It is well-known that fluorescent X-rays, scattering X-
rays, photoelectrons in addition to fluorescent X-rays when X-rays are irradiated onto solids. In addition to these radiations, infrared-ultraviolet-rays are emitted depending on materials, and they are called “X-ray excited optical luminescence (XEOL)”. Since a spectrum of this luminescence is sensitive to the chemical state of the mate-
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ment is possible for light elements using XEOL [21].

VII. CONCLUSION

In the present article, I state our recent achievements on XFH. Nowadays, transmission electron microscopy (TEM) or scanning probe microscopy (SPM) is routinely used in scientific and industrial fields. However, they provide only shadow or surface image, and cannot offer the 3D atomic arrangements. In contrast to these methods, XFH has a great advantage to visualize 3D atomic images within few nm. For this, we have applied the XFH to clear the local
structure around dopants in single crystals. In addition to this, recently we found that the XFH can evaluate local lattice distortion in mixed crystals. We are now developing a new XFH apparatus with a cryostat, which can measure holograms at a sample temperature of 5 K. Using this system, materials exhibiting interesting features at very low temperature, such as highly correlated electron system.

As related methods to the XFH, there are photoelectron holography, γ-ray holography [22] and neutron holography [23]. The photoelectron and γ-ray holography can choose emitter atoms not only by element but also by chemical state. Neutron holography can image hydrogen nuclei, and therefore, it will be useful for structural analyses of hydrogen storage materials. Moreover, since the amplitude of the neutron magnetic scattering is similar to that of the nucleus scattering, we can explore magnetic materials with the neutron holography. These atomic resolution holography methods have great potentials, and possibly their performances will be improved in near future. Hereafter, we can obtain new knowledge of structures of unknown materials by applying these methods.

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