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# Applications of X-ray fluorescence holography to determine local lattice distortions

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ABSTRACT

X-ray fluorescence holography (XFH) is a method for investigating atomic order up to the medium ranges, and can provide 3D atomic images around specific elements within a radius of nm order. In addition to these characteristics, XFH is sensitive to positional fluctuations of atoms, and therefore it is useful for characterizing the local lattice distortions around specific elements. We have applied XFH to dopants and mixed crystals. We found interesting features in local lattice distortions, such as the displacements of first-neighbor atoms around dopants, far-sighted views of the atomistic fluctuations in mixed crystals, and the coexistence of distorted/undistorted sites in the same material.

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## 1. Introduction

X-ray fluorescence holography (XFH) [1] is a relatively new local structural analysis method, which can determine atomic arrangements around a specific element without any prior knowledge of structures. It can directly reconstruct 3D atomic images using Fourier transformation. We consider that XFH and the related atomic resolution holographic techniques (photoelectron holography, neutron holography) are a third method of structural analysis at the atomic level after X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS). As known by many researchers, XRD and XAFS are established methods that are widespread use in various fields. XRD and XAFS provide information on long-range translational periodicities and very local environments, respectively, whereas XFH gives 3D information on the local order and can visualize surrounding atoms with a large range of coordination shells. Such characteristics are major advantages of XFH.

XFH only requires samples with orientational order. For example, to determine the structure of a molecule, we must orient the molecules on a substrate as illustrated in Fig. 1. However, a sample with long-range periodicity, such as a crystal, is not necessary, in contrast to XRD. XFH is very powerful for determining local structures around dopants [2]. XAFS is also frequently used for the analysis of local structures. It provides one-dimensional radial distribution functions around specific elements and can accurately determine the interatomic distances and coordination numbers of the first to third neighbor shells. In contrast, XFH provides 3D atomic images within a diameter of several nm order. From the viewpoint of structural analysis, this novel feature of XFH has a strong possibility of opening new fields in solid-state physics. To date, using XFH we have obtained new information on the structures of some advanced materials. We call this feature of XFH "3D medium-range local structure observation".

Finding novel nanometer clusters is one of the major advantages of XFH. For example, in 2009, we studied the phase transition behavior of $Ti_{50}Ni_{44}Fe_6$ single crystal, a shape-memory-alloy related material. This material exhibits parent (P), incommensurate (IC), and commensurate (C) phases when the temperature is decreased to below room temperature. While the atoms in $Ti_{50}Ni_{44}Fe_6$ are distributed homogeneously in the P-phase, they formed cluster-like structures with a radius of 8 Å in the C-phase, where the motion of the atoms inside the clusters is frozen. This is valuable information for understanding the phonon softening at the phase transition [3].

In addition to the feature of "3D medium-range local structure observation", XFH is very sensitive to the displacement of atoms from their ideal positions, and one can obtain quantitative information about local lattice distortions by analyzing reconstructed atomic images [4]. When dopants with different atomic radii from

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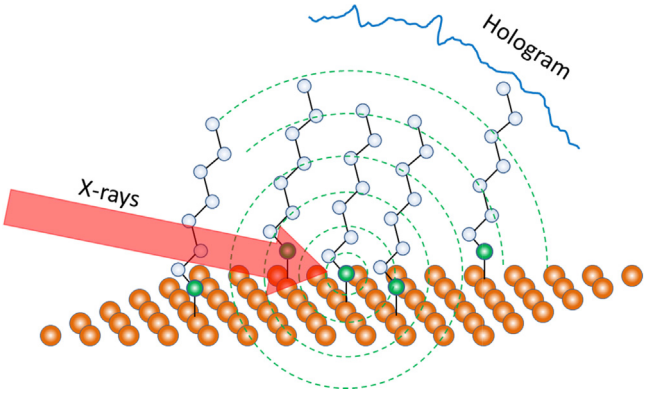


**Fig. 1.** Concept of X-ray fluorescence holography.

the matrix elements are present, the lattices around the dopants are distorted. However, using the conventional methods of structural analysis, one cannot determine the extent to which the local lattice distortions are preserved from the dopants. XFH is a good tool for solving this problem. The present article is a review of our results obtained by the study of local lattice distortions.

## 2. History

The well-known Kikuchi [5] and Kossel [6] lines are two-dimensional patterns formed by the diffraction of photoelectrons and fluorescent X-rays produced by internal point sources in single crystals. They were first reported in the 1920s and 1930s, respectively, and have been used to evaluate the crystallinity of single crystals. Although the Kossel and Kikuchi lines are now considered to be parts of the holograms of the XFH and photoelectron holography, this was not pointed out until 1986 by Szöke [7]. Since his suggestion, atomic-resolution holography has developed rapidly with the improvements of strong X-ray sources and detectors.

Since the amplitudes of photoelectron holograms are 20–50% of the background amplitude, the holograms can be easily measured. Therefore, the first atomic-resolution holography was realized using photoelectrons in 1990 by Harp et al. [8]. An XFH experiment was performed by Tegze and Feigel to demonstrate its use for the structural analysis of strontium titanate ($SrTiO_3$) [9]. A few months of measurements were, however, required to record a single hologram using a commercial X-ray generator (X-ray tube) and a solid-state X-ray detector owing to the weak holographic oscillations of 0.1–0.01% relative to their background intensities. They measured the spherically distributed fluorescence intensity while varying the detector position, a method known as normal XFH. From this experiment, they found that a strong X-ray source is necessary to record XFH holograms in a reasonable measurement time. Therefore, the focus of XFH soon moved to the use of synchrotron radiation facilities.

Shortly after the above demonstration of XFH, Gog et al. introduced a different mode of XFH, inverse XFH [10]. In this mode, a hologram is obtained from the angular integrated fluorescence intensity as a function of the incident beam direction. Since inverse XFH holograms can be recorded at any energy above the absorption edge of a target element, one can obtain holograms of the same sample at many different energies. This is highly advantageous for eliminating the twin-image effect, which is an inherent problem of single-energy holograms.

Nowadays, using a combination of a strong synchrotron radiation X-ray beam and a very fast detector, the measurement time of XFH has been reduced to only 3 h. An atomic image with a resolution of ~0.5 Å has been achieved [11], and even light elements such as oxygen can be displayed owing to the use of a data set with extremely high statistical quality [12]. Additionally, a specific surrounding element can be detected using a resonant X-ray scattering technique. Moreover, reliable 3D images can be reconstructed over a very wide range with a nm-order radius. As mentioned above, these features make it possible to analyze medium-range local structures and to provide more valuable information than that obtained by XAFS, which provides only short-range local structures.

Since XFH requires samples with a regular atomic orientation, amorphous or polycrystalline samples cannot be used. However, this does not mean that samples should be perfect single crystals. We can apply XFH to partially disordered single crystals, such as clusters, surface adsorbates, quasi-crystals [13], and impurities. Moreover, our XFH group has recently found XFH to be highly advantageous for investigating medium-range local structures such as lattice distortions in mixed crystals and cluster formations in phase transition materials.

## 3. Principles

As mentioned above, there are normal and inverse [10] modes in XFH. Fig. 2 shows the principles of these two modes using a dimer as the simplest model. In the normal mode shown in Fig. 2(a), atom A is excited by a primary X-ray and emits fluorescent X-rays. Part of the fluorescent X-ray wave is scattered by the neighboring atom B. The scattered and unscattered fluorescent photons respectively serve as object and reference waves. These two waves interfere at a position far from the sample and modulate the intensity on a spherical surface surrounding the sample. The hologram is thus measured as variations in the intensity of the fluorescent X-rays.

In this process, the path difference between the reference and object waves is $d(1-\cos\theta)$, where $d$ is the interatomic distance between A and B and $\theta$ is angle BAC in Fig. 2(a). The phase of the fluorescent X-ray is shifted by $\pi$ when scattered by the atoms owing to the negative charge of the electrons. Thus, the intensity is maximized when $d(1-\cos\theta)/\lambda$ is equal to a half-integer, where $\lambda$ is the wavelength of the fluorescent X-rays. Using the atomic scattering factor of atom A, $f(\theta,\lambda)$, the relative intensity of fluorescence, $I(\theta,\lambda)$, can be expressed as

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

where $r_e$ is the classical electron radius. Since the atomic scattering cross section for X-rays is extremely small, the magnitude of the second term is less than $10^{-3}$. Therefore, Eq. (1) can be approximated as

$$I(\theta,\lambda) \cong 1 - Re\left(\frac{\lambda r_e f(\theta,\lambda)}{2\pi d} e^{i2\pi d(\cos\theta-1)/\lambda}\right) \quad (2)$$

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

Fig. 2(b) shows the principle of the inverse mode, which is based on the idea of the optical reciprocity of the normal mode. An incident X-ray wave directly approaching atom A (reference wave) is interfered with by the wave scattered by atom B (object wave), which results in the formation of an X-ray standing wave field around atom A. The pattern of the X-ray standing wave varies with the direction of the incident X-ray beam, which results in the angular dependence of the X-ray fluorescence intensity from atom A. This angular variation is equivalent to that of the hologram in the normal mode, and the normalized intensity of the fluorescence can also be expressed as Eq. (2). Since inverse XFH allows recording at any incident energy above the absorption edge of an emitter element, clear atomic images without ghosts can be obtained owing

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