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Local crystal structure analysis with several picometer precision using scanning transmission electron microscopy

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ABSTRACT

We report a local crystal structure analysis with a high precision of several picometers on the basis of scanning transmission electron microscopy (STEM). Advanced annular dark-field (ADF) imaging has been demonstrated using software-based experimental and data-processing techniques, such as the improvement of signal-to-noise ratio, the reduction of image distortion, the quantification of experimental parameters (e.g., thickness and defocus) and the resolution enhancement by maximum-entropy deconvolution. The accuracy in the atom position measurement depends on the validity of the incoherent imaging approximation, in which an ADF image is described as the convolution between the incident probe profile and scattering objects. Although the qualitative interpretation of ADF image contrast is possible for a wide range of specimen thicknesses, the direct observation of a crystal structure with deep-sub-angstrom accuracy requires a thin specimen (e.g., 10 nm), as well as observation of the structure image by conventional high-resolution transmission electron microscopy.

1. Introduction

Conventional transmission electron microscopy (CTEM) and scanning transmission electron microscopy (STEM) are effective for analyzing a local crystal structure. In comparison with CTEM, annular dark-field (ADF) imaging in STEM has several advantages for material characterization. ADF imaging is considered to be incoherent imaging, in which the obtained image can be described as a convolution between the intensity profile of an incident probe and a compositionally sensitive object function [1,2], resulting in high compositional sensitivity and intuitive interpretability. The features of incoherent ADF imaging and coherent CTEM imaging are very different; the former is less dependent on optical parameters (e.g., defocus of the objective lens) and diffraction conditions (e.g., specimen thickness). ADF imaging is thus a promising method for local crystal structure analysis.

The quantitative analysis of ADF images, however, has the following experimental difficulties. One is the quantum noise, i.e., a low signal-to-noise (SN) ratio, because it utilizes low-intensity high-angle scattering. The other is the marked image distortion due to specimen or/and incident probe drift. Although these drawbacks are reduced using a spherical aberration (*Cs*) corrector, the inherent performance of ADF imaging has not yet been fully realized. In our previous works, we improved the energy resolution in electron energy-loss spectroscopy (EELS) using software-based techniques such as drift correction and deconvolution [3,4]. On the basis of these techniques for EELS, we also developed a STEM instrument and related software techniques [5–9] because the two methodologies are based on the same convolution model. Here, we report a comprehensive procedure for performing local crystal structure analysis using STEM. We present several software-based techniques for experiments and data processing, which are applicable for *Cs*-corrected STEM. We also point out the limitation of the proposed method, which is related to the validity of the incoherent imaging approximation of STEM–ADF.

2. Experimental

We used a dedicated scanning transmission electron microscope (HD-2300C, Hitachi High-Technologies) equipped with cold field emission gun (CFEG) and DigiScan (Gatan) [7]. The accelerating voltage is 200 kV and the spherical aberration coefficient is 0.57 mm, resulting in the Scherzer incoherent resolution [2] of 0.13 nm. The microscope is highly stabilized, e.g., the specimen drift rate in this experiment is less than 0.3 nm/min. The probe current is 4.4 pA and the convergence semiangle is 15 mrad. The bright-field (BF) detector semiangle is 5 mrad. The ADF detector

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inner angle is set to 36 mrad, which is relatively small compared to that for *Cs*-corrected STEM, to acquire sufficient ADF intensity. We confirmed that ADF images with an inner angle of 36 mrad show *Z*-contrasts [6,9]. The source size on the specimen is roughly estimated to be 0.03 nm assuming a CFEG virtual source size of 5 nm and a demagnification of 1/150; therefore the effect of the source size (e.g., as described in [10]) is not significant in comparison with the minimum probe size of this STEM. The BF and the ADF detector signals are measured using the DigiScan, whose background offsets are carefully calibrated. We have prepared experimental and data-processing software based on DigitalMicrograph (DM) script (Gatan). Examples of DM scripts are described elsewhere [3].

We observed a $TmFeO_3$ single-crystal specimen. The crystal structure of $TmFeO_3$ is gadolinium orthoferrite, $GdFeO_3$ type [11], which has recently attracted much attention because of its magnetic properties [12,13]. $GdFeO_3$ structure is considered to be a modified perovskite structure ABO_3, in which the *A*-site position is substantially modulated. Its space group is Pnma: a=0.5571 nm, b=0.7582 nm and c=0.5249 nm. In this study we observe $TmFeO_3$ along the [0 0 1] direction, which corresponds to the [1 1 0] direction of a primitive perovskite structure. The TEM specimen was prepared by mechanical thinning and low-voltage ion milling using the GentleMill (Technoorg LINDA).

A multislice simulation program (xHREM, HREM Research, Inc.) was also used for quantitative analysis [14,15]. The above-mentioned crystallographic parameters were used in the simulation. The Debye–Waller factor B of $TmFeO_3$ has not been reported; therefore, we approximately used the B factor of $GdFeO_3$, which has the same crystal structure and the most similar atomic number: B(Tm,Fe,O)=(0.19, 0.10, 0.77). Although the B factor is related to the ADF intensity, the major feature of the incident probe propagation, which is the main topic of this study, depends on elastic scattering; therefore, the approximate B parameter is applicable for the analysis of the atom position measurement.

3. Procedure and experimental results

3.1. Outline of the procedure

The proposed procedure consists of (i) experimental techniques and (ii) data-processing techniques. The former includes multiple fast acquisition and specimen drift tracking. The latter includes drift correction, the estimation of defocus and specimen thickness, resolution enhancement by deconvolution and a peak search. In the following section, we describe each technique in detail with a few experimental results.

3.2. Multiple fast acquisition with drift tracking

STEM images with a high SN ratio are required for realizing high precision. To improve the SN ratio, we acquired many BF and ADF images (100 each) using a customized DM script. The dwell time and the number of pixels were 0.005 ms and 512×512 pixels, respectively. The total acquisition time for 200 images was 371 s. BF and ADF images are alternately acquired, i.e., quasi-simultaneous acquisition is performed. The quasi-simultaneous acquisition of BF and ADF images is necessary in this study because of the following two reasons. First, the BF image is used for specimen thickness evaluation, which is described in Section 3.4. Second, we can estimate specimen drift using BF images even if the ADF images suffer poor SN ratio.

If an instrument is not sufficiently stabilized, the specimen drift during multiple acquisition exceeds the original scanning area, resulting in an out-of-range failure. We measured the relative drifts of sequential STEM images by cross correlation during the acquisition, and the scanning area was shifted to counterbalance the measured drifts, i.e., drift tracking. The translational symmetry in crystals is problematic in the estimation of the relative shift because of the multiple peaks in the cross-correlation patterns of the crystallographic images. We have to optimize the experimental conditions (e.g., pixel size and dwell time) to keep the relative drift within half of the projected unit cell size. Otherwise, the data processing becomes translational averaging, which differs from *local* crystal structure analysis. It is, however, worth mentioning that the translation averaging is another effective software-based approach to analyze an *average* crystal structure with a high precision [16,17].

3.3. Post-acquisition drift correction

Since the drift tracking does not perfectly eliminate specimen drift, we perform post-acquisition drift correction. Relative drift is evaluated by the cross correlation between the first image and other images, because the subpixel shifts would be accumulated if we used the cross correlation of sequential STEM images. Since each specimen drift in BF and ADF images is evaluated individually, we can double-check the estimated specimen drifts by comparing them. We occasionally apply a convolution (e.g., 3×3 smoothing) before calculating the cross correlation for the noise reduction. Since the convoluted images are used only for drift measurement, the experimental data after the drift correction is still raw data.

Fig. 1 shows BF and ADF images of $TmFeO_3$ with the crystal structure model after post-acquisition drift correction. In the ADF image, Tm and Fe atomic columns are observed as bright and less bright dots, respectively. In the BF image, cation sites are not clearly observed owing to dynamical diffraction. Generally, it is difficult to find the corresponding atomic sites in conventional BF images; however, we can overlap the crystal structure because we simultaneously observed the ADF image.

STEM images often suffer cyclic noise owing to stray electromagnetic fields at mains frequency and/or mechanical vibration of rotating equipment (e.g., turbo molecular pump). The amplitude of such noise in recent STEM scanning systems is smaller than the spatial resolution of the systems; however, the noise is often apparent in STEM images as fine stripes, and is also visible in the Fourier transform (FT) of the STEM image as duplicated spots far from the center of the FT pattern. The effect of the cyclic noise can be effectively reduced by this drift correction. This is also effective for reducing erroneous contrast changes owing to the instability of the probe current (e.g., the tip noise of a CFEG).

A high SN ratio image is essential for distinguishing between atomic columns with a similar *Z* number, and also for detecting low-intensity objects in the image such as the signal of a dopant atom in matrix materials [9]. The precision in the measurement of peak positions in the ADF is improved; for example, we demonstrated the reduction of the standard deviation in interatomic distance measurement from 18 to 8 pm [8]. Using time-series observation, we can also investigate damage to a specimen as a function of incident electron dose.

3.4. Defocus evaluation using ADF image

The optical parameters and diffraction condition should be determined for precise analysis by STEM. In the case of BF imaging in CTEM, many parameters, such as defocus and specimen