Direct Imaging of a Local Thermal Vibration Anomaly Through In-situ High-temperature ADF-STEM

Anomaly Through In-situ High-temperature ADF-STEM

Introduction

Anomalous dark-field scanning transmission electron microscopy (ADF-STEM) provides atomic-resolution images by effectively illuminating each atomic column one-by-one as a finely focused electron probe \((\sim 2 \text{ Å})\) is scanned across the specimen, due to the fact that the fast incidence-electrons propagate along the atomic columns with strong channeling effects, generating an intensity map at the annular detector \((\text{Fig. 1})\). To a good approximation, the atomic-resolution in ADF-STEM is interpreted to be a result of independent intensity measurements of electrons scattered from individual atomic columns, and hence the observed intensity distribution \((I(R))\) can be simply described by a convolution between a probe-intensity function \((P(R))\) and a scattering object function \((O(R))\) \((\text{incoherent image})\) [1]:

\[
I(R) = O(R) \otimes P(R)
\]

Here, \(O(R)\) represents the columnar scattering cross-section that contributes to the annular detector. By detecting sufficient high-angle scatterings \((s > \sim 1 \text{ Å}^{-1})\); see \(\text{Fig. 2}\), the intensity at the detector is dominated by phonon scattering events; that is, thermal diffuse scatterings \((\text{TDS})\). An Einstein model of independently vibrating atoms is valid enough to describe the high-angle diffuse scatterings. Therefore, the TDS intensity can be practically treated by an absorptive form factor given as an attenuation of the elastic scattering by the Debye-Waller \((\text{DW})\) factor, whose high-angle approximation is well described by the TDS cross section \((\sigma_{\text{TDS}})\) effective to the annular-detector range [1]:

\[
f_{\text{as}}(M, s) = \sigma_{\text{TDS}} \propto \int_{s_{\text{ann}}} \int_{s_{\text{ann}}} f(s) [1 - \exp(-2M \cdot s)] ds^2 (2)
\]

where \(f_{\text{as}}(M, s)\) is the absorptive atomic form factor for high-angle scatterings and the \(f(s)\) is the atomic form factor for elastic scatterings \((\text{with} s = \theta/2, \theta \text{ is a scattering angle,} \lambda \text{ is the electron wave-length and} M \text{ is the DW factor defined by mean-square thermal vibration amplitude of the atoms. Therefore, the intensity of each illuminated atomic column will be directly dependent on the} \sigma_{\text{TDS}} \text{ within the relevant column. We note that TDS described by} \sigma_{\text{TDS}} \text{ is sufficient for estimating the integrated intensity reaching the detector, although it does not reflect any fine details} [2] \text{ of the high-angle diffraction pattern.}

Since the TDS intensity is proportional to the square of \(f(s)\) \((\text{Eq. (2)})\), the ADF-STEM provides a significant atomic-number dependent contrast \((Z\text{-contrast})\) which has been quite useful to determine the local chemical structures at atomic scale. In addition to this amplitude sensitive nature of ADF-contrast, it should be reminded that the \(f_{\text{as}}(M, s)\) or \(\sigma_{\text{TDS}}\) is a function of both \(M\) and \(s\) \((\text{see the upper-right hand side in} \text{ Fig. 1})\); ADF-contrast is also sensitive to the DW factors at individual atomic sites. With this in mind, we here describe the first direct imaging of a local thermal vibration anomaly in a solid [3], through in-situ heating/cooking \((\text{and angle-resolved})\) ADF-STEM experiments.

STEM Experiment

ADF-STEM was performed by a JEM-2010F \((\text{URP version with spherical aberration Cs=0.5 mm})\) equipped with a scanning unit [4]. The minimum probe is approximately \(\sim 1.5 \text{ Å}\) with a convergence angle of \(\sim 12 \text{ mrad}\), and it can reveal clearly the dumb-bell feature of the GaAs structure, as shown below in Fig.1. Samples for STEM observation were prepared by dispersing crushed alloys on perforated carbon films supported on copper grids; by this method, surface amorphous layer, roughness, and contamination that are frequently induced by ion-milling and strongly affect the ADF contrast can be avoided. In-situ atomic-resolution ADF-STEM observation at 1100K was achieved using a heating holder \((\text{JEOL EM-31050})\) that does not require any water-cooling during the observation even at 1100K.

ADF-STEM Observation of Al72Ni20Co8 Quasicrystal

The structure of quasicrystals – having long-range order with symmetries that are incompatible with periodicity – is often described with reference to a higher-dimensional analogue of a periodic lattice [5]. Within the context of this ‘hyperspace’ crystallography, lattice dynamics of quasicrystals can be described by a combination of lattice vibrations and atomic fluctuations – phonons and phasons. The phason is an extra elastic degree of freedom that may cause

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an anomalous fluctuation at specific atomic sites, and the DW factor of a quasicrystal can be written as:

\[ M = M_{\text{phonon}} + M_{\text{phason}} \]  

(3)

Here we present the direct observation of local anomalies of the DW factor in a quasicrystal, through an in-situ high-temperature ADF-STEM observation on a decagonal Al\(_{72}\)Ni\(_{20}\)Co\(_{8}\) for which a nearly-perfect, ideal quasiperiodic structure can be obtained by annealing at 1100K (the thermodynamically stable phase). In the observation at room temperature (300K: Fig. 3 (a)), the ADF-STEM image highlights the transition metal (TM : Ni or Co) positions relative to the Al due to the \( f'(s) \) dependence of the contrast (Eq. (2)). But when the sample is heated and held at a temperature of approximately 1100K in the microscope, we find a remarkable change in the relative contrast; compare Fig. 3 (b) to Fig. 3 (a). It is evident that a significant enhancement in contrast appears at some specific places that can be well represented by the pentagonal quasiperiodic lattice with an edge-length of 2 nm. Further, we notice that the anomalous ADF-contrast occurs at cores of the decagonal cluster (Fig. 3 (b)) which is a structural unit of the decagonal Al\(_{72}\)Ni\(_{20}\)Co\(_{8}\) [6]. A representative feature of the clusters is shown in Figs. 4 (a) and (b).

Viewing carefully the interior contrast of the decagons, an increase of intensities is found to be significant at the positions indicated by arrowheads, which are the Al sites in the decagonal cluster model (Fig. 4 (c)). The intensity profiles show that the Al atom at the core, denoted as Al\(_c\), in fact shows stronger contrast at 1100K than that at 300K. We confirmed that this temperature-dependence contrast change is reversible; that is, after cooling down to 300K from 1100K, the anomalous contrast regions become darker again. It should be noted that the intensity at the Al\(_c\) site (\( I_{\text{Al}_c} \)) is originally stronger than that of the other Al sites at 300K (Fig. 4 (a)); the \( I_{\text{Al}_c} \) is confirmed to vary significantly depending on the angular range of the detector [3]. These angular-dependent as well as temperature-dependent (reversible) anomalous ADF-contrast can naturally be attributed to a local anomaly of the DW factor, as expected through Eq. (2); assuming that the DW factor effect is equivalent for all the Al sites, neither of these dependences is expected. We interpreted the significant increase of \( I_{\text{Al}_c} \) in terms of atomic vibration amplitudes, \( u^2 \), and successfully showed that the observed anomalous ADF-contrast at the Al\(_c\) site is clearly correlated with differences in \( u^2 \) [3]. This is, to our best knowledge, the first direct observation of a local vibration anomaly in a solid. The local anomalies of \( u^2 \) presently observed imply significant anharmonicity at the Al\(_c\) site. Similar anomalies might therefore be anticipated at the neighboring TM sites, and some evidence of this is seen at 1100K (Fig. 4 (b)). Here it is quite interesting to note that the Al\(_c\) sites, located at the center of the decagonal clusters that are on the 2 nm-scale pentagonal quasi-periodic lattice vertices, are shown to be phason-related according to the hyperspace crystallographic description [7]. Thus, the present local DW factor anomaly indicates an occurrence of phasonic fluctuations – a perturbation of a quasiperiodic order that can be described...
through $M_{\text{phason}}$ (Eq. (3)) – realized for the Al\textsubscript{\textgreek{s}} atoms. An occurrence of DW factor anomalies at the Al\textsubscript{\textgreek{s}} site is probably induced by the presence of the phason-flip atomic sites, denoted as $\beta$ in Fig. 4 (c), which are separated by less than a typical interatomic distance. These $\alpha$ and $\beta$ sites cannot be occupied simultaneously, and the $\beta$ sites, considered to be energetically similar to the Al\textsubscript{\textgreek{s}} site, could act as vacancies in providing an effective space for relaxation; it is very reasonable to assume that this causes a significant anisotropy in the DW factor, as illustrated in Fig. 4 (c), although the resolution of the present STEM (~1.5 Å) is not sufficient to reveal this anisotropic behavior. At high temperatures, occasional diffusion atomic jumps between the $\alpha$ and $\beta$ sites are naturally expected (Fig. 4), causing phason-related structural disorders.

**Summary**

The present work demonstrates the additional capabilities of ADF-STEM – not only to provide Z-contrast, it can be used to detect a local thermal vibration anomaly in a solid by doing in-situ heating/cooling and/or the angle-resolved experiments. Further quantitative determination of the DW factor at each atomic site would be possible by comparing carefully the angle-dependent ADF-contrast change with the calculated intensity that includes both the elastic and TDS scatterings reaching the given angular range of the detector.

**References**