Synchrotron X-ray Studies of Phason and Phonon Strains in a Co-rich Al-Ni-Co Decagonal Quasicrystal

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1. Introduction

The peak broadening and peak shifts of Bragg reflections, caused by some characteristic strains, are of great interest in studies of the stability of quasicrystals and the mechanism of transformation from a quasicrystal phase to an approximant crystal phase. The linear phason strain produces peak shifts that increase monotonically with the physical momentum $Q$. On the other hand, the phonon strain monotonically increases with the physical momentum $Q$. In the measurements of peak broadening and peak shifts, the synchrotron X-ray diffraction method provides quantitative estimations of phason and phonon strains. For example, high-resolution synchrotron powder X-ray measurements of Al-Cu-Ru icosahedral alloy performed by Guryan et al. shows the peak broadening depending to the physical momentum $Q$. They concluded that the peak broadening is well accounted for by the simple lattice (phonon) strain, with no measurable dependence of the FWHM on the phason momentum $Q$. Synchrotron X-ray studies with decagonal single crystals were first performed for the Al-Cu-Co decagonal quasicrystal by He et al. They concluded that the Al-Cu-Co decagonal quasicrystal was certainly phason-free because the FWHMs of the Bragg reflections peaks have no $Q$ dependence. Since then, many synchrotron single-crystal X-ray studies have been carried out for quasicrystals [e.g., 3–5].

Recently, we performed synchrotron single-crystal X-ray studies with extreme high-resolution on beam line BL02B1 at SPring-8 for Al$_70$Ni$_{10}$Co$_{20}$ (S1-type) decagonal quasicrystal. In these observations, the FWHM of the Bragg reflections along the longitudinal direction could exhibit linear $Q$ dependence without the deconvolution of the slit resolution.

Here, the Al-Ni-Co decagonal phase has various types of superstructures and modulation, which change with the temperature and/or compositions. Recently, various studies of the construction of the phase diagram were carried out for Al-Ni-Co involving the decagonal phase. Ritsch et al. have constructed a precise phase diagram and shown that at least eight types of decagonal phases exist over wide temperature and composition ranges. And the structures of these types have been studied by atomic-scale observations of high-angle annular detector scanning transmission electron microscopy (HAADF-STEM), for basic Ni-rich, S1-type, S1$_{15}$-type-I superstructure, type-II superstructure, and 5f$_{15}$ phases. These examinations, however, were mainly conducted by electron diffraction and electron microscopy techniques.

Therefore, the purpose of the present work is to obtain detailed information of peak profiles and to estimate the quantitative phason strain and phonon strains for an Al$_{72.7}$Ni$_{8.5}$Co$_{18.8}$ decagonal phase that is different in composition from the above-mentioned Al$_{70}$Ni$_{10}$Co$_{20}$ decagonal phase by using the high-resolution synchrotron X-ray diffraction method. We have already reported X-ray studies of successive transformation from a decagonal quasicrystal through one-dimensional quasicrystal to an approximant quasicrystal at an Al$_{72.7}$Ni$_{8.5}$Co$_{18.8}$ composition. In the decagonal phase of the Al$_{72.7}$Ni$_{8.5}$Co$_{18.8}$ composition, the coexistence of random phonon strains with phonon strains was observed. However, the quantitative estimation of the coexistence has not been performed. Therefore, we present detailed information for peak profiles and qualitatively analyze the coexistence of random phonon strains with phonon strains in the Al$_{72.7}$Ni$_{8.5}$Co$_{18.8}$ decagonal phase.

2. Experiment

An alloy ingot with a nominal composition Al$_{72.7}$Ni$_{8.5}$Co$_{18.8}$ was prepared by melting high purity Al(99.99%), Ni(99.99%), and Co(99.99%) in an Ar atmosphere using an arc furnace. This ingot was crushed into powder, placed in an arc furnace, and melted under Ar atmosphere. The liquid was held for 15 minutes at a temperature of 1750°C. After holding, the sample was rapidly cooled at a rate of 10$^3$ °C/s to ensure a complete quenching at room temperature. The ingot was crushed into powder, placed in an arc furnace, and melted under Ar atmosphere again. This process was repeated several times.

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alumina crucible, and sealed in a quartz tube. The powder specimen was remelted at 1373 K and slowly cooled to 1123 K at a rate of 1 K min\(^{-1}\). After being annealed at 1123 K for 24 h, the specimen was quenched in water. A needle-like single crystal with decaprismatic morphology (1 mm × φ0.2 mm) was picked up for X-ray diffraction experiments.

Conventional X-ray diffraction experiments were carried out using monochromated MoK\(α\) radiation with a four-circle diffractometer (Rigaku AFC-5). The MoK\(α\) radiation was monochromated by a graphite(002) crystal. Measurements were made for the diffraction geometry using a crystal orientation with the tenfold axis parallel to the \(ϕ\)-axis and perpendicular to a scattering plane. In order to measure precisely both the position and the FWHM of the diffraction peak in a \(Q\)-step scan along the longitudinal direction (L-direction), which corresponds to the \(2\theta-ω\) scan, a high resolution was achieved using a sharp slit with a horizontal width of 0.15 mm, which was set at a 257 mm distance from the sample. In this monochromator and slit system, the experimental momentum resolution along the L-direction is \(2.3 \times 10^{-2}\) nm\(^{-1}\).

On the other hand, to achieve an extremely high-resolution, synchrotron X-ray diffraction experiments were performed on beam line BL02B1 at SPring-8. An off-centered (Huber) 7-circle diffractometer was installed in this beam line. The synchrotron beam was monochromated by Si(311) double crystals to give energy of 20.00 keV. The corresponding X-ray wavelength was 0.0620 nm. The detailed peak shapes and peak positions of Bragg reflections were measured in the manner as mentioned above. The receiving slit, which had a width of 0.20 mm, was set at a 900 mm distance from the sample. In this slit system, the experimental momentum resolution along the L-direction is \(0.30 \times 10^{-2}\) nm\(^{-1}\).

In this paper, we calculate reciprocal momentums \(Q_{||}\) and \(Q_{⊥}\) correspond to \(Q = 1/d = 1/\sin θ \text{ without } 2π\).

### 3. Results and Discussion

In this article, we adopt the same indexing scheme as was used by He et al.,\(^2\) where the first five integers indicate the quasiperiodic plane and the last one indicates the periodic direction. In the present experiment, the last integer was kept to zero and omitted.

Precise measurements for the peak profile and positions of the Bragg peaks have been carried out using conventional X-ray diffraction and high-resolution synchrotron X-ray diffraction methods. Hereafter, two kinds of the twofold symmetry axes in the quasiperiodic plane are referred to as the (10000) and (01001) directions, using a five-dimensional (5D) indexing scheme. Figure 1 shows the conventional X-ray diffraction patterns along the (10000) (a) and (01001) (b) directions and their calculated peak positions using the five-dimensional lattice parameter \(A_{5D} = 0.6261(6)\) nm, which is

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**Fig. 1** X-ray diffraction patterns along the (10000) (a) and (01001) (b) directions and calculated peak position.
estimated from three strong peaks indexed as (10220), (20330), and (03223). As shown in the figures, all peaks are very sharp and indexed as the decagonal phase. The peak profile of each Bragg reflection could be fitted by symmetric Gaussian functions with $K\alpha_1$ and $K\alpha_2$ components. From the ideal Bragg positions, all of the peak shifts are estimated, but no notable ones were observed over the experimental momentum resolution of $2.3 \times 10^{-2}$ nm$^{-1}$. The FWHMs of Bragg peaks observed with the conventional X-ray diffraction method are plotted against $Q_1$ in Fig. 2. In this figure, there are two lower limit lines with constant and linear dependences with $Q_1$. The former depends on the slit resolution, and the latter is produced by phonon strains. The zigzag discrepancies from these lines are produced by random phonon strains. When the random and isotropic distribution of both the phonon and phonon strains is considered, the FWHM of the Bragg reflection depends on both $Q_1$ and $Q_\perp$, as written by $\Delta Q^2 = \alpha^2 Q_1^2 + \beta^2 Q_\perp^2 + \gamma^2$, where $\alpha$, $\beta$, and $\gamma$ are parameters [e.g., 1.5,12]. For the slit system in a conventional X-ray experiment, $\gamma$ has a momentum resolution of $2.3 \times 10^{-2}$ nm$^{-1}$. The least squares fit yields $\alpha = 0.0029(2)$ and $\beta = 0.0011(2)$ with $R = 0.075$, where $R = \Sigma |\Delta Q^{\text{obs}} - \Delta Q^{\text{cal}}|/\Sigma \sqrt{(\Delta Q^{\text{obs}})^2} - \gamma^2$. Each parameter has a large error, and the realistic function $R$, excluding the effort of the slit resolution, is not small enough. Therefore, with a conventional X-ray diffraction method, it would be difficult to make a precise estimate of the phonon and phonon strains for an Al$_{12.7}$Ni$_{18.5}$Co$_{18.8}$ decagonal phase.

On the other hand, high-resolution synchrotron X-ray measurements can identify substantial peak profiles and perform a quantitative estimation of phonon and phonon strains. Measurements were carried out from $Q_1 = 1.0$ nm$^{-1}$ to $Q_1 = 12.5$ nm$^{-1}$ with a suitable step size and integral time for each peak. The maximum value of $Q_1$ for measured peaks is $2.264$ nm$^{-1}$ for the (10220) reflection. In Figs. 3(a)–(d), typical peak profiles along the L-direction for the (00110), (20000), (20440), and (30220) reflections are respectively shown. The (00110) peak with a small $Q_1$ value of 1.638 nm$^{-1}$ and a small $Q_\perp$ value of 0.626 nm$^{-1}$ is fitted by a symmetrical Lorentzian function with a narrow FWHM of $0.0053$ nm$^{-1}$. The peak with small $Q_1$ and $Q_\perp$ values is slightly affected by both the phason and phonon strains. Therefore, the profile of the (00110) peak is close to the intrinsic one depending on the apparatus used in these synchrotron X-ray measurements. The (20000) peak with a small $Q_1$ value of 2.025 nm$^{-1}$ and a large $Q_\perp$ value of 2.025 nm$^{-1}$ is fitted by a symmetrical Lorentzian function with a broad FWHM of 0.0133 nm$^{-1}$. Because the peak with small $Q_1$ and large $Q_\perp$ values is mostly affected by phonon strains, symmetrical Lorentzian broadening of Bragg peaks along the L-direction is produced by the phonon strains. The (20440) peak with a large $Q_1$ value of 8.578 nm$^{-1}$ and a small $Q_\perp$ value of 0.478 nm$^{-1}$ has an asymmetrical profile. The peak intensity has a remarkable tail on the low-angle side, but it drops rapidly on the high-angle side. The profile on the high-angle side is similar to a single Lorentzian profile. Because the peak with large $Q_1$ and small $Q_\perp$ is mostly affected by phonon strains and all peaks with a large $Q_1$ value show similar features along the L-direction, the phonon strain has a non-random distribution in this sample. This asymmetrical peak can be suppositionally fitted by two Lorentzian peaks with the same FWHM. One of them is located at the peak position, and the other is located in the tail with smaller intensity. Therefore, the single crystal may be constructed with two kinds of grains that have $A_{\text{SP}}$ values of 0.6273 and 0.6265 nm, and the same ordered phonon strains. Otherwise, the single crystal may have merely non-randomly distributed phonon strains. The third possibility is an intermediate state between the above-mentioned ones. Accordingly, to analyze the convolution of phonon and phonon strains simply, the FWHM of each asymmetrical peak is estimated from a Lorentzian peak located at the Bragg peak position. Here, the (20440) peak shows an FWHM of 0.0106 nm$^{-1}$. The (30220) peak with a large $Q_1$ value of 6.940 nm$^{-1}$ and a large $Q_\perp$ value of 1.786 nm$^{-1}$ has an asymmetrical Lorentzian peak with a broad FWHM of 0.0148 nm$^{-1}$. This peak is equally affected by both the phonon and phonon strains. The above-mentioned features could be observed in both the (10000) and (01001) directions.

The peak shifts from the ideal Bragg positions for all peaks were precisely estimated, but no notable peak shifts were observed over the experimental momentum resolution of $0.3 \times 10^{-2}$ nm$^{-1}$. The FWHMs of the Bragg peaks were precisely estimated by the above-mentioned peak fitting. The dependence of the FWHM against $Q_1$ is plotted in Fig. 4. As can be seen in Fig. 4, there is a lower limit line with a linear dependence with $Q_1$ and a zigzag with respect to the lower limit line. The effect of the slit resolution is very small. When the random and isotropic distribution of both the phonon and phonon strains is considered, the FWHM of the Bragg reflection depends on both $Q_1$ and $Q_\perp$, as written by $\Delta Q^2 = \alpha^2 Q_1^2 + \beta^2 Q_\perp^2 + \gamma^2$, where $\alpha$, $\beta$, and $\gamma$ are parameters [e.g., 1.5,12]. In this study, $\gamma$ is the momentum resolution of 0.003 nm$^{-1}$. The least squares fit yields $\alpha = 0.0012(2)$ and $\beta = 0.0067(25)$ with $R = 0.115$, where $R = \Sigma |\Delta Q^{\text{obs}} - \Delta Q^{\text{cal}}|/\Sigma \sqrt{(\Delta Q^{\text{obs}})^2} - \gamma^2$. The square of deconvoluted FWHM against the square of $Q_1$ is plotted in Fig. 5. In this figure, the systematic discrepancy is observed. This reason is explained as follows. For a convolution of Gaussian functions, a square of convoluted FWHM is a sum of each
square of FWHM. On the other hand, for a convolution of Lorentzian functions, a convoluted FWHM is a sum of each FWHM. In our high-resolution synchrotron X-ray measurements, each peak has Lorentzian form as shown Figs. 3(a) to (d), and the momentum resolution of the slit system, which shows Gaussian contribution to peak broadening, is enough small compared with observed FWHMs of each peak. From these features, the above-mentioned model due to a con-

Fig. 3 Peak profiles along the L-direction for the (00110) (a), (20000) (b), (20440) (c), and (30220) (d) peaks.

Fig. 4 FWHM as a function of $Q_\parallel$ estimated from synchrotron X-ray diffraction peaks. Filled and open circles denote the (10000) and (01000) directions.

Fig. 5 The square of deconvoluted FWHM as a function of the square of $Q_\perp$. The solid line is the calculated dispersion given by the least squares fitting based on $\Delta Q^2 = \alpha Q_\parallel^2 + \beta Q_\perp^2 + \gamma^2$. 

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revolution of Gaussian functions is insufficient for estimating the phason and phonon strains quantitatively in this experiment. Therefore the fitting model due to a convolution of Lorentzian functions should be applied instead.

According to this indication, if the function, written by 
\[ \Delta \theta = \alpha Q_1 + \beta Q_1 + \gamma \]

is assumed, the least squares fit yields \( \alpha = 0.0095(8) \) and \( \beta = 0.0054(3) \) with \( R = 0.047 \), where \( R = \Sigma|\Delta Q_{bs} - \Delta Q_{al}|/\Sigma(\Delta Q_{bs} - \gamma) \). The deconvoluted FWHMs are plotted against \( Q_{\perp} \) and \( Q_\parallel \) in Figs. 6(a) and 6(b), respectively. As can be seen in Fig. 6(a), the deconvoluted FWHM against \( Q_{\perp} \) has a clear linear dependence. Therefore, the latter fitting model would be a more reasonable choice for quantitatively discussing the phason and phonon strains using the high-resolution synchrotron X-ray measurement.

From above mentioned analysis, the peak broadening against \( Q_{\perp} \) is characterized by the same linear dependence of FWHM along the two directions of (10000) and (01001) as shown in Fig. 6(a) and the asymmetrical peak profile as shown in Fig. 3(c). Therefore, the phonon strain in this quasicrystal is characterized by isotropic but non-random distribution.

To measure the strength of the phason strain component, Boudard et al.53 compared the observed broadening with the distortions of the diffraction pattern resulting from a linear phason strain for Al-Pd-Mn icosahedral quasicrystals. We applied their method to the decagonal quasicrystal. The peak shift by the linear phason strain is given by

\[ \Delta Q_{\parallel} = M \cdot Q_{\perp}, \]

where \( M \) is a phason matrix as follows

\[ M = \begin{pmatrix} \theta_1 & 0 \\ 0 & \theta_2 \end{pmatrix}. \]

A Co-rich Al-Ni-Co decagonal quasicrystal shows successive phase transformations at the same composition from the decagonal phase through a one-dimensional quasicrystal to an approximant crystal.15,16 The approximant crystal has the phason matrix components, \( \theta_1 = -0.02 \sim -\tau^{-8} \) and \( \theta_2 = 0.014 \sim \tau^{-7} \), corresponding to a unit cell, \( a = 6.105 \) nm and \( b = 5.193 \) nm, respectively.15 On the other hand, the one-dimensional quasicrystal phase has the phason matrix components \( \theta_1 = -0.02 \sim -\tau^{-8} \) and \( \theta_2 = 0 \). These phason matrix components correspond to a periodicity, \( a = 6.105 \) nm.16 The random phason strain component \( \beta = 0.0054 \sim \tau^{-11} \) is much smaller than the absolute values of both \( \theta_1 \) and \( \theta_2 \) for the approximant crystal and \( \theta_1 \) for the one-dimensional quasicrystal phase. Therefore, the random phason strains included in this decagonal phase are not directly related to successive phase transformations.

4. Conclusion

Synchrotron X-ray diffraction experiments have given quantitative estimations of random phason strains and phonon strain in the decagonal Al_{72.7}Ni_{8.3}Co_{10.6} quasicrystal classified as the 5f state. The coexistence of random phason strains with phonon strains was observed in this decagonal crystal. The phason strain shows random and isotropic distributions, and the value of the random phason strain component is \( 0.0054 \sim \tau^{-11} \). On the other hand, the phonon strain shows isotropic but non-random distributions, and the single crystal may be constructed with two kinds of grains that have \( \gamma_{3D} \) values of 0.6273 and 0.6265 nm.

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