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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Single crystal X-ray study of decagonal quasicrystals and the approximant in Al-Ni-Rh system	**Experiment number**: 01-02-934
Beamline:	**Date of experiment**: from: 9 April 2011 to: 12 April 2011	**Date of report**: 20.02.2012
Shifts: 9	**Local contact(s)**: Volodymyr Svitlyk (email: svitlyk@esrf.fr)	*Received at ESRF:*

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Report:

Abstract

The aim of the experiments was to perform single crystal X-ray diffraction studies of 2 new decagonal quasicrystal phases (with a period of 4 Å and 16 Å along the 10 –fold axis) and an approximant (with a period of 16 Å along the pseudo-decagonal axis) formed in Al-Ni-Rh system. Synchrotron radiation was required to collect enough both weak and strong reflections for successful structure determination and refinement.

Experimental

Synchrotron single crystal diffraction experiments were carried out at the Swiss Norwegian Beamline (ESRF) using the KUMA KM6-CH single crystal diffractometer equipped with a CCD area detector. The measeured decagonal quasicrystals and the approximant were obtained at different temperatures from the melt with nominal composition $Al_{71}Ni_{15}Rh_{14}$.

Since datasets collected on quasicrystals contain many of weak reflections, an accurate instrumental parameter file is of primary importance to allow a reliable integration of those reflections. First rough estimates for instrumental parameters had been obtained from the refinement based on a dataset collected on spherical ruby. Those estimates were further used as starting values for more accurate instrument parameters refinements based on a dataset collected on a large unit cell cubic zeolite crystal. The obtained instrumental parameter file was used for refining the orientation matrix of the measured decagonal quasicrystal.

To acquire enough strong and weak reflections for structure solution and refinement two datasets with increment of 0.10 deg. and resolution of 0.6 Å were collected for each crystal. During the first dataset collection the intensity of the primary beam had been adjusted to allow integration of all the strongest reflections. During collection of the second dataset all strongest reflections were overexposed in favour of obtaining intensities of more weak reflections. Intensities of the reflections collected during both runs were

ploted versus each other. Only reflections along the linear part of the plot were used for determination of the scale factor between two datasets by means of a least squares refinement. The scaled datasets have been merged together before averaging. All the experiments proceeded without technical problems.

For all the measured crystals a significant number of reflections could be acquired. The datasets were merged with an internal *R*-values of around 5 %. Reflection integration and data reduction was performed using the software package CRYSALIS (Oxford Diffraction). The structure was solved using SUPERFLIP [1] , a program for performing iterative phase-retrieval methods like charge flipping [2] and low-density elimination.

Results

The crystal structure of the approximant was refined using a 3-dimensional approach and software SHELX [3]. The refinement in space group *Pnma* resulted in $R1 = 0.0328$ for 5791 reflections with $I_{obs} > 2\sigma(I_{obs})$ and 0.0731 for all 10311 reflections. The refined composition is $Al_{72}Ni_{10.5}Rh_{17.5}$. It was found that Ni and Rh form mixed occupied sites, whereas no mixing of Al and Ni was found.

The crystal structure of the 4Å decagonal phase was refined in 5-dimensional space using QUASI07_08 [4], a package for multidimensional least-squares refinements. The refinement was carried on in space group $P10_5/mmc$ and resulted in $R1=0.063$ for 1100 reflections $I_{obs} > 2\sigma(I_{obs})$ and 0.097 for all 2238 reflections. The reined chemical composition of the quasicrystal corresponds to the formula $Al_{70}Ni_{16.5}Rh_{13.5}$.

For this structure it was found that both Rh and Al form mixed occupied sites with Ni. Both structures show significant positional disorder around some of the Al-positions. For the quasicrystal disorder is more prominent, what probably originates from the fact that its crystal structure is stabilized at higher temperatures than that of the approximant. Having high quality synchrotron data with many acquired weak reflections was absolutely crucial for the refinements. Both structures have similar structure motifs. In particular, they share the same type of Rh-Al-clusters formed around Rh-atoms. The presence of those clusters allows validating a part of the model for the studied quasicrystaline phase.

Both refined chemical compositions are in a reasonable agreement with the composition obtained from the EDX analysis

It has to be highlighted that the presented crystal structure of 4 Å-decagonal quasicrystal belongs to one of the first solved and refined structures of the ternary quasicrystals, where all three atom types could be distinguished based on their significantly different scattering factors.

The manuscript based on the obtained results is currently under preparation. The analysis of the crystal structure of 16 Å-decagonal phase is in progress.

The undertaken X-ray diffraction measurements on the decagonal phases show their either 4 or 16 Å periodicity along 10-fold axis, whereas the lattice period of the approximant along the pseudo-10-fold axis is 16 Å. Both, the synthesis conditions and the relation between the unit cell parameters suggest that the obtained materials transform one into the other upon cooling and have related crystal structures.

We are planning to submit another proposal aimed to study that transformation, which might shed some light on the yet unclarified reason of stability of quasicrystals.

References

(1) L. Palatinus, G. Chapuis, *J. Appl. Cryst.* **2007**, 40, 786-790.
(2) G. Oszlanyi, A. Suto, *Acta Crystallogr.* **2007**, A60, 134-141.
(3) G.M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112–122.
(4) S. Weber, A. Yamamoto, *Philos. Mag.* **1997**, A*76*, 85-106.