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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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:** Precise diffraction pattern measurements of decagonal Al-Cu-Me (Me = Co, Rh, Ir) quasicrystals.	**Experiment number**: **HS- 4292**
Beamline:	**Date of experiment**: from: 06/04/2011 to: 09/04/2011	**Date of report**: 17/02/2012
Shifts: 9	**Local contact(s)**: Volodymyr SVITLYK	*Received at ESRF:*

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Report:

Experiment:

Single crystal X-ray diffraction experiments of three decagonal phases (Al-Cu-Co, Al-Cu-Rh and Al-Cu-Ir) were performed at SNBL (BM 01A), using KUMA KM6-CH diffractometer equipped with the Titan (Agilent Technologies) CCD detector (wavelength 0.69800 Å, oscillation angle 0.1^{o}). For each crystal two data sets were collected (3 835 frames each), one dataset with short exposure time to prevent saturation of the strong reflections, second with long exposure time to acquire a large number of weak reflections (strong reflections saturated). All datasets covered the full sphere up to 0.6 Å resolution to achieve accurate merging and absorption correction. Additionally a standard large-unit-cell reference crystal was measured once every 18-24 hours. This is essential for proper integration of quasicrystal data. The instrumental parameters cannot be easily refined based on the diffraction data from aperiodic crystal alone. Therefore one has to supply the instrumental parameters for integration obtained from a high quality reference crystal diffraction data. Since the instrumental parameters may slightly change over time, it is crucial to repeat the standard crystal measurements. All experiments ran very smoothly and no technical problems occurred.

Results:

For each crystal both datasets (long and short exposure times) were combined, scaled and merged in the $10/mmm$ Laue class. This resulted in very large datasets (over 1500 independent reflections with $I/\sigma > 3$) with satisfying internal R-values below 0.05. The diffraction pattern of a quasicrystal consists of only a few strong reflections and large number of weak reflections carrying important structural information. Therefore synchrotron measurements providing large, high quality datasets, are a must for a reliable structure refinement of a quasicrystalline structure.

The datasets were initially phased using the charge flipping algorithm (Oszlanyi & Suto, 2008) and computer program SUPEFLIP (Palatinus & Chapuis, 2007). All structures show two layer periodicity i.e. there are two quasiperiodic layers within one period along the *c* axis (periodic axis). According to the chosen space group the layers are related by the 10_5 screw axis. Based on the physical space sections of the electron density maps, Penrose tiling based models were derived. Penrose tiling is a geometrical 2D structure build of two units (thick and thin rhombuses), which is perfectly long-range ordered yet aperiodic. It also exhibits local 5-fold symmetry and therefore it is a natural candidate for a *quasilattice* for the description of a quaiscrystalline structure.

The structure refinement was conducted in the physical space only using the so-called Average Unit Cell (AUC) approach described extensively in (Wolny *et al.*, 2002, Kozakowski & Wolny, 2010). In order to use this approach one needs the atomic decoration of the rhombic unit tiles and proper symmetry constraints for the decoration (according to the chosen space group). The AUC method has already been successfully used for structure refinements of various decagonal phases in the Al-Ni-Co system (Wolny *et al.*, 2008, Kuczera *et al.*, 2010, Kuczera *et al.*, 2011).

The refinements resulted in the first solution of a decagonal quasicrystal as a real ternary alloy. The mass difference of the constituent elements (in case of Al-Cu-Ir and Al-Cu-Rh samples) allowed to distinguish all three atomic species in the structure. For investigated quasicrystals the resulting chemical composition agrees well with the EDX measurements and the final *R*-values are reasonable. The manuscript of a paper presenting our results is under preparation and is expected to be soon submitted to Acta Crystallograhica B.

The follow-up proposal to SNBL will be submitted in the running call (March 2012 deadline). Within our proposed project we are planning to study the thermal stability of the Al-Cu-Rh and Al-Cu-Ir quasicrystals. Since their discovery, the question whether quasicrystals are mainly energy or entropy stabilized never could be answered clearly. Experimental support for both, in some way, contradictory, mechanisms can be found in literature. We plan to perform temperature dependent X-ray diffraction measurements and to solve the crystal structures of Al-Cu-Rh and Al-Cu-Ir decagonal quasicrystals at different temperatures.

References:

Kozakowski, B. & Wolny, J. (2010). *Acta Crystallogr A* 66, 489-498.
Kuczera, P., Kozakowski, B., Wolny, J. & Steurer, W. (2010). *J Phys Conf Ser* 226.
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