EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Structure of the (100) surface of the orthorhombic $Al_{13}Co_4$ crystal, approximant to the decagonal quasicrystalline phase	**Experiment number**: SI2316
Beamline: ID03	**Date of experiment**: from: Sep. 28th, 2011 to: Oct. 5th, 2011	**Date of report**:
Shifts: 21	**Local contact(s)**: R. Felici, J. Drnec	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

É. Gaudry, L. Serkovic-Loli, G. McGuirk, J. Ledieu, V. Fournée, Institut Jean Lamour, UMR 7198 CNRS – Université de Lorraine, Nancy, France.

M. de Boissieu, G. Beutier, SIMaP: Sciences de l'Ingénierie, des Matériaux et des Procédés, Grenoble INP, CNRS, UJF, France.

G. Renaud, CEA et ESRF, Grenoble, France.

J. Drnec, R. Felici, ID03, ESRF, Grenoble, France.

Report:

The aim of the experiment was the precise structural determination of the (100) surface of the $Al_{13}Co_4$ crystal, which is an approximant to decagonal quasicrystalline phases and an efficient and highly selective hydrogenation catalyst for alkynes [1,2]. The surface structure determination is essential to gain (i) a complete understanding of the surface plane selection in complex metallic alloys in comparison to what occurs in quasicrystals and (ii) a correct structural surface model required for further chemical reactivity studies. The orthorhombic o-$Al_{13}Co_4$ crystal belongs to the $Pmn2_1$ (oP102) space group and its unit cell contains 102 atoms [3]. It has lattice parameters equal to a = 0.8158 nm, b = 1.2342 nm and c =1.4452 nm. The structure of the o-$Al_{13}Co_4$ phase can be described by the stacking of flat (F) and puckered (P) layers along the [100] direction with a pseudo 10-fold symmetry. They appear in the sequence $F_{0.0}P_{0.25}F_{0.5}P_{0.75}$ where $P_{0.25}$ and $P_{0.75}$ are mirrored against $F_{0.5}$. The average interlayer spacing is 0.202 nm. The surface unit cell contains 22 Al and 4 Co atoms in P layers and 17 Al and 8 Co atoms in F layers.

The (100) surface of the $Al_{13}Co_4$ approximant has been investigated by a combination of methods, including STM, XPS, dynamical LEED and *ab initio* calculations using density functional theory (DFT) [4-7]. A concensus has emerged that the surface terminates at P layers only. However, a controversy persists whether the terminating plane is a complete or an incomplete P-layer. The main objectif of the SXRD experiment is to discriminate amongs these models.

A single crystal has been grown by the Czochralski method from Al-rich solutions and properly oriented by back-Laue scattering. A clean surface has been prepared in the ID03 UHV end station by repeated sputtering (Ar+, 1 kV) and annealing cycles (up to 850 °C). A large number of Crystal Truncation Rods (CTRs) have been measured using the six-circle diffractometer up to the largest reachable in-plane and out-off plane momentum transfer, while keeping the incident angle close to the critical angle for total external reflection. An energy of 15 keV was chosen, well above the absorption edges of Co to avoid counting the fluorescence, but not too high to avoid too large diffuse scattering from the bulk. All together, over 200 reciprocal lattice

rods have been measured. The data set was collected in the interval of L: $0.9 \leq L < 4.9$. The analysis of this large data set is in progress, as described below.

The first step was to extract the experimental structure factors from diffraction images (see Fig. 1). Diffraction images often had inhomogeneous backgrounds, so choosing a reliable yet not too tedious subtraction procedure (given the rather large data set) was necessary. We have tested different sized background subtraction windows over two ranges of L-values; at each (h,k) point, four perpendicular l-index values closest to the surface were recorded and saved as a single set of images. We found that choosing subtraction windows optimized for each L-value was time-consuming and did not highlight features better than using a single window for all four L-values. To choose this window, we first examined the complete image set for each rod to identify defect intensities and non-uniform background reflections. Then, the window was minimized with a perimeter having the smallest pixel intensity gradient, which excluded as many defects as possible while including important surface features adjacent to each L-value.

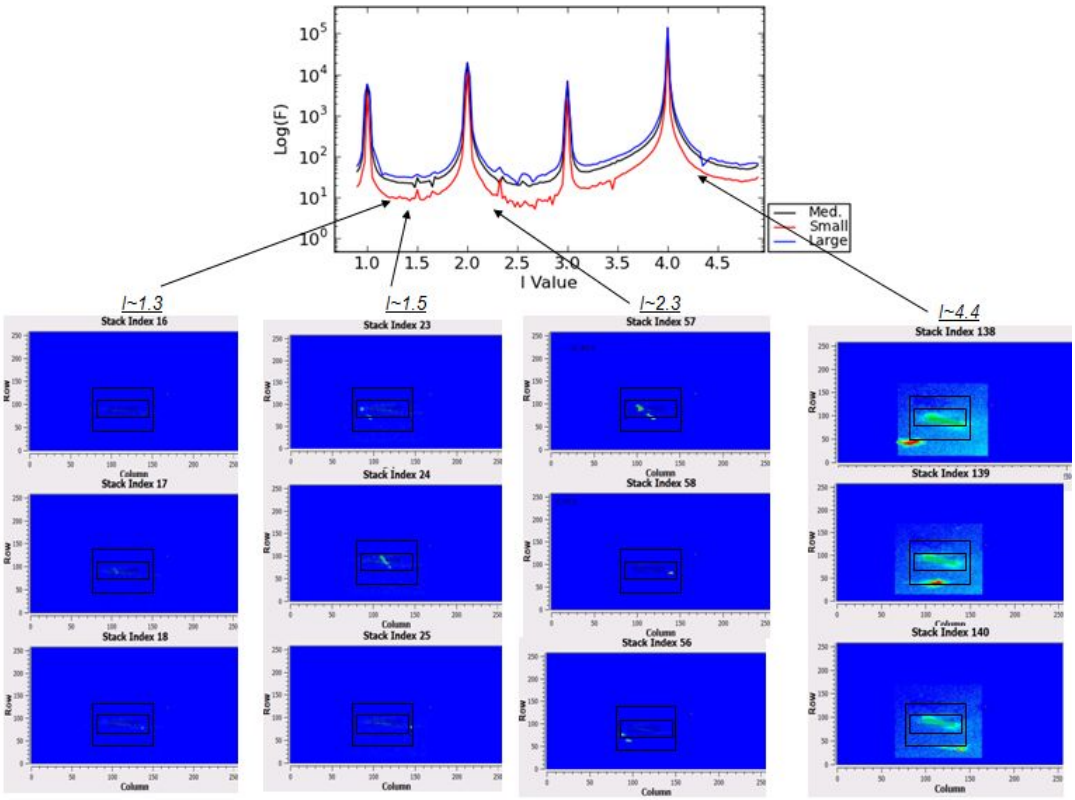

Fig. 1: The graph above shows differences in experimental structure factors (F), obtained upon intensity integration of SXRD images with different background subtraction windows. The image windows shown in the three left columns are examples of defects. The column on the far right shows how both defects and background inhomogeneity effect the slope next to integer L-values (l=4 in this case). Note that the small integration window is shaded-in (without a solid black border), so that image features are not blocked.

Fig.1 shows an example of three different sized windows obtained using the "Integration NON specular EH2 final.py" background subtraction plug-in for PyMCA. Using this script and medium-sized windows, similar to the one shown above, eliminated defect intensity while preserving the asymmetric features adjacent to integer L-values necessary for SXRD surface structure analysis. Furthermore, after coordinating with beam-line scientists, we also tested two other background subtraction algorithms and decided to use the plug-in mentioned above. Next, we extracted the experimental structure factor of over 200 reciprocal lattice rods and compared all symmetric rods. Many were ill-defined due to exceptionally large background reflections and defects, so data were narrowed down. Data of the useful symmetric rods were more carefully re-extracted with each having identical background subtraction window positioning and area. Following this, spikes were removed from data and the well-defined rods were compiled together to construct a .INT file.

The next step is to sort out and average the data using the AVE software. The standard deviations σhkL of the structure factor amplitudes |FhkL| were evaluated by the squared sum of a systematic error, estimated to be close to 8%, and of the statistical error. A plane group symmetry P1 was selected. Averaging leads to a .DAT file to be fitted using ROD and a .FIT file.
Several .FIT files were contsructed based on the various surface models as in [5]. The surface consists of either a complete P1+P2 termination, with or without the Co atoms, or incomplete P1+P2 termination containing only one set of bientagonal motifs, with or without Al glue atoms (see [5]). So far, only a limited number of rods have been included into the .DAT files. The quality of the fit is estimated by the value of χ^2 and its normalized value N. For all these models, we find a similar value of N ~6 and a reasonnable quality of the fit as shown in Fig. 2 for several CTRs. The data analysis is still in progress with the help of experts from the beamline but first results are encouraging and demonstrate that surface x-ray diffraction analysis on such structurally complex is feasible.

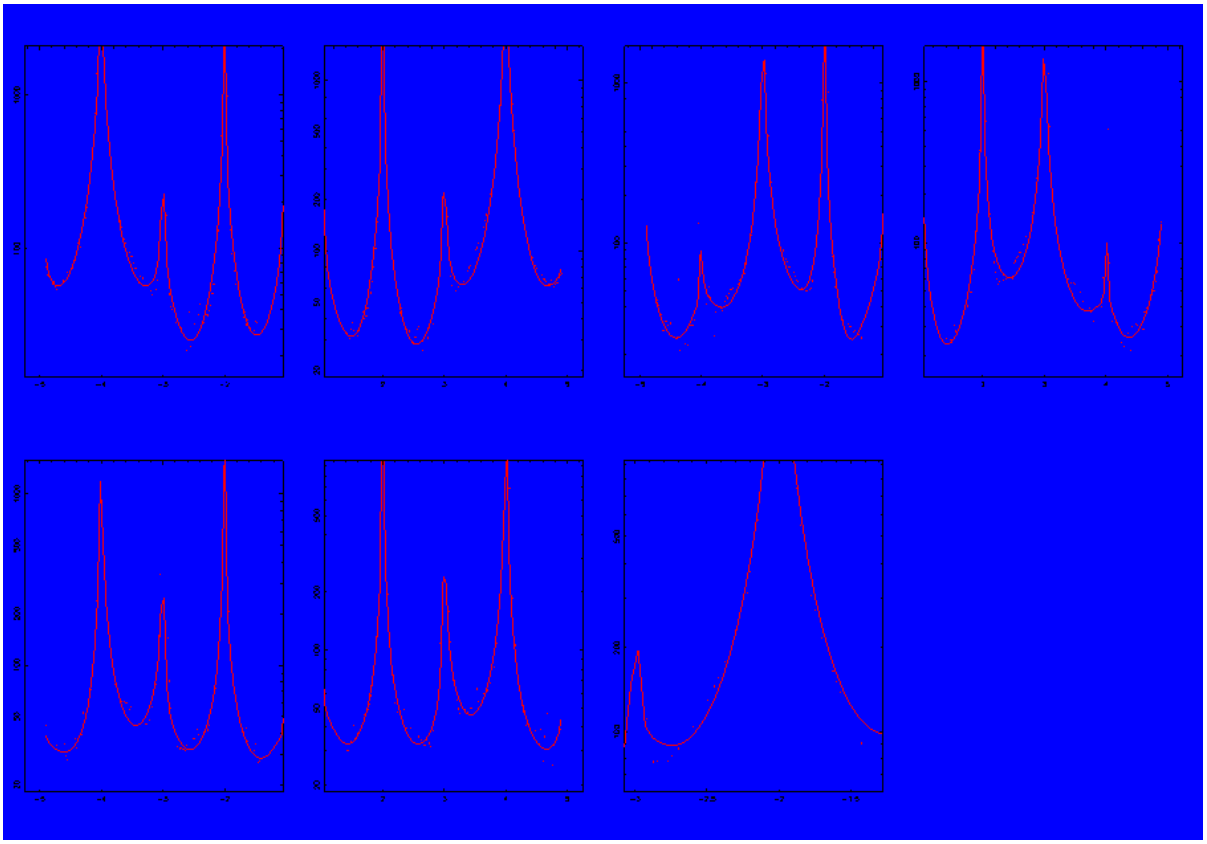

Fig. 3. Measured (dotted lines) and calculated (solid lines) structure factors amplitudes versus index L for several CTR. Here the complete P1+P2 model has been used.

References:

[1] M. Armbrüster, K. Kovnir, Yu. Grin, R. Schlögl, P. Gille, M. Heggen, and M. Feuerbacher, European Patent No. EP09157875.7 2009.
[2] M. Armbrüster, K. Kovnir, M. Friedrich, D. Teschner, G. Wowsnick, M. Hahne, P. Gille, L. Szentmiklósi, M. Feuerbacher, M. Heggen, F. Girgsdies, D. Rosenthal, R. Schlögl, and Yu. Grin, Nat. Mater. 11, 690 (2012).
[3] J. Grin, U. Burkhardt, M. Ellner, and K. Peters, J. Alloys Comp. 206, 243 (1994).
[4] R. Addou, E. Gaudry, T. Deniozou, M. Heggen, M. Feuerbacher, P. Gille, O. Groening, V. Fournée, J.M. Dubois, J. Ledieu, Phys. Rev. B, 80 014203 (2009).
[5] H. Shin, K. Pussi, É. Gaudry J. Ledieu, V. Fournée, S. Alarcon, P. Gille, W. Moritz, R. D. Diehl, Phys. Rev. B, 84, 085411 (2011).
[6] M. Krajči and J. Hafner, Phys. Rev. B, 84, 115410 (2011).
[7] V. Fournée, É. Gaudry, M. C. de Weerd, R. D. Diehl and J. Ledieu., MRS proceedings 2012.