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*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** Diffuse scattering in the Ba(1-x)LaxF2(1+x) and Rb2ZnCl4 crystals	**Experiment number**: HC 4742
Beamline: ID28	**Date of experiment**: from: 8.09.21 to: 14.09.21	**Date of report**: 10/09/2021
Shifts:	**Local contact(s)**: Alexei Bosak	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

X- Ray diffraction experiments and diffuse scattering experiments were performed on Rb2ZnCl4 on the side station of ID28. Single crystal of size ~0.1mm was mounted on a goniometer head within a capillary which is then mounted on a Huber diffractometer with euler geometry. PILATUS3 1M hybrid pixel detector was used to detect the scattered X-rays. Given the Kα (~13 keV) and Kβ (~15 keV) edges of 'Rb', the wavlength $\lambda = 0.5226$Å (~23.72 keV) - Si(12 12 12) was used for the experiment to avoid the flourescence along with a lower threshold (~17 keV) for the Pilatus detector. Rb2ZnCl4 is incommensurately modulated at room temperature with a q-vector (1/3-δ) c* , as it approaches the lock-in transition at 192K 'δ' becomes close to zero. Therefore, inorder to have a good resolution so that we can separate main and satellite reflections well enough, a large sample-to-detector distance of 244 mm was used. Two different 2θ offsets, a lower one (19°) and a higher one (48°) were used because of the long distance and different atteuators were used for data collection to detect both strong main refections and weak satellite reflections. Data was collected at several temperatures and these temperatures were maintained with the help of heat blower for high temperatures (~350K) and Oxford Cryostream with Nitrogen gas for lower temperatures (upto 90K). The diffraction images were collected employing 'Phi' scans with steps of 0.1° and with an exposure time of 0.2 seconds per image. Therefore, a complete dataset at each temperature had runs of 3600 images with two different 2θ-offsets and different attenuators. Apart from full data collection, data was also collected during temperature ramps i.e heating and cooling, to get an idea on phase transitions. At every 0.5K/1K steps near the transition temperature, 500 images were collected corresponding to 50° phi rotation around a bragg peak of interest. For diffuse scattering measurements, exposure time of 0.6 seconds per frame was used instead of 0.2 seconds and without any attenuation.

Starting with room temperature, data was collected at 293K, 300K, 350K along with the temperature scans (data collection during the ramp) while heating and cooling. One can see from the reconstructed reciprocal space images (Fig. 1) that the satellites slowly disappear as the T increases with traces of diffuse scattering. Similarly while cooling, diffuse scattering slowly intensified at satellite positions and finally turned into bragg peaks at 293K . With the help of varied peak intenisties obtained from the temperature scans, the phase transition from

Normal to Incommensurate phase is determined to be around 295K while the reported transition is around 303K. This could be due to the heating of the sample by the high flux incident beam.

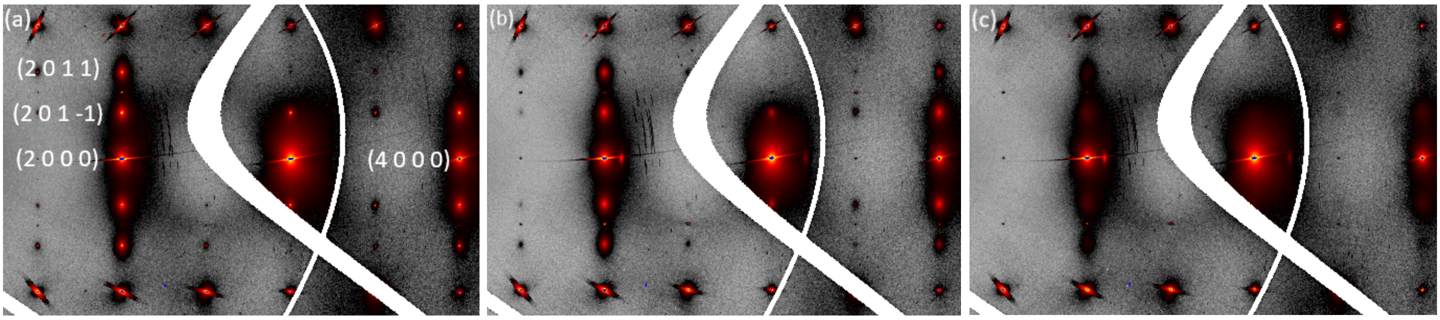

Fig. (1) Reciprocal space H0L planes (a) 293K (b) 300K (c) 350K

From 293K, going down the temperature in the incommensurate phase the satellites became stronger and slowly, higher order satellites started appearing (Fig. 2). At 200K satellites upto 5th order and higher are observed and this is due to the change in behaviour of modulation from a harmonic sinusoidal one at high temperature to a highly anharmonic modulation near the lock-in temperature. This region near the lock-in transition (~192K) is the focus area for current experiment and thus complete datasets were collected at 275K, 250K, 225K, 200K and temperature scans were collected around the bragg reflection (6 0 0) and nearby satellites. The evolution of higher order satellites with temperature can be seen in Fig. 2 where the c* axis is in the horizantal direction. A line scan along this bragg reflection clearly shows the higher order satellites (Fig. 3) , The peaks indicated with an '*' are due to the multiple scattering.

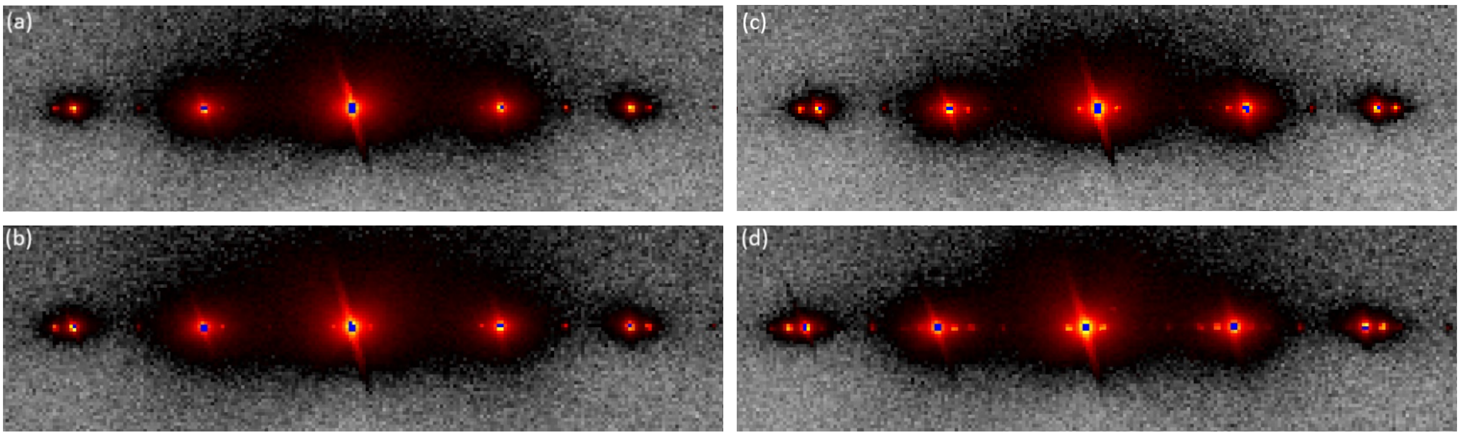

Fig. (2) Reciprocal space H0L planes (a) 275K (b) 250K (c) 225K (d) 200K

From the temperature scans it was evident that q-vector decreased with temperature and slowly the satellite reflections came closer to each other. However, even below the reported lock-in transition temperature the reflections didn't merge, still showing the incommensurability. Continuing t-scans further down the temperature, around 160K, satellite reflections appeared to merge, showing commensurate nature with 1/3 q -vector. This difference arised might be due to the heating of the sample by the incident beam similar to what has been observed at Incommensurate transition. The results were consistent with a repeated cycle of heating and cooling. Moreover, change in lattice parameters with different attenuation foils used for data collection also indicated the effect of incident beam radiation on the crystal. Other factors such as crystal defects and ramp rate might also weigh in. The t-scans were furthur continued until 90K and a complete dataset was collected at 90K which now had sharp superlattice reflections confirming the commensurate phase.

However, further analysis of X-Ray diffraction data collected in the incommensurate phase should be helpful to understand the evolution of modulation with the temperature and the diffuse scattering measurements which were even prominent in the lock-in phase should be useful to understand the lattice dynamics.

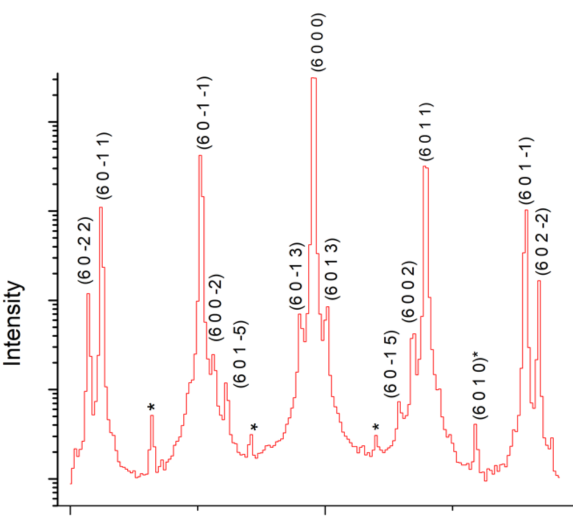

Fig. 3