EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Charge-density waves in quasi-one dimensional M2Mo6Se6 (M=Rb, Tl) studied by polarised XAS	**Experiment number**: 28-01-1175
Beamline: BM28	**Date of experiment**: from: 26/10/2016 to: 01/11/2017	**Date of report**: 3/5/2017
Shifts: 18	**Local contact(s)**: Laurence Bouchenoire and Paul Thompson	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Background: Two samples were measured during the allocated beamtime, $Rb_2Mo_2Se_6$ and $Tl_2Mo_6Se_6$. Both materials form a uniaxial hexagonal structure, with space group P63/m, where $(Mo3Se3)_\infty$ chains run along the c-axis. The guest ions in between the chains is Rb in one case and Tl in the other. It is known that these crystals are non-stoichiometric, with vacancies on the interstitial sites but the chains are highly crystalline. These two materials belong to a family of quasi-1D systems with interesting properties and that tend to be borderline beweeen superconducting and insulating transitions. $Rb_2Mo_6Se_6$ in particular is insulating at low temperatures and shows a resistivity upturn with a resistance minimum between 100 and 250 K, depending on the sample. $Tl_2Mo_6Se_6$ is a conducting material that tunrs superconducting at ~ 6 K but also shows anomalies on the transport measurements (upturn in thermopower, zero-crossing of the Hall coefficient at ~80 K). The formation of charge density waves (CDW) has been suggested for both materials as a possible explanation of their conducting properties. However, there has been no direct evidence of the formation of CDW in any diffraction or ARPES data collected so far. The results from these measurements exclude the formation of long-range-ordered distortions in these materials. The experiment we carried out at BM28 was designed to probe the presence of short-range lattice distortions in $Rb_2Mo_6Se_6$ at temperatures below the minimum in the resistance for this material (~100K). This scenario is compatible with theoretical calculations of the structure, which suggested that a twist-mode rotation of the Mo_3 triangles was energetically favourable in this material. $Tl_2Mo_6Se_6$ should not undergo that type of transition in that temperature range and can hence be used as a reference (although this second sample could potentially also show a structural transition at lower temperatures).

Experiment: we carried out the experiment on small, needle-like single crystals (see Fig. 1 for an example) of approximately 3mm x 0.25mm. We used a He4 cryostat with a Be dome to control the temperature over the required range and a Vortex Si-drift diode as our detector. We concentrated most of our measurements on the Se K-edge (12,6578 keV) and measured up to 1,000 eV over the absorption edge to cover both the XANES and EXFAS regions. We also collected some test data at the Mo K-edge as a feasibility test. We found that data could be collected and the beam was stable but, as expected, the flux was significanlty suppressed. It would have taken us more than factor of 3 longer to collect data at the Mo K-edge if we wanted to obtain comparable statistics with respect to the Se K-edge. We concluded that for this specific experiment that was not a good use of beamtime and did not pursue measurements in this energy range. The crystals available for the experiment were of good quality but small with respect to the beam size; hence the measurements were sensitive to beam/sample stability, not to the point that it would stop us from collecting good and reproducible data but it did mean that the useful range of data was more limited at the higher energy (or *k*) range than it could have been if larger crystals had been avaible.

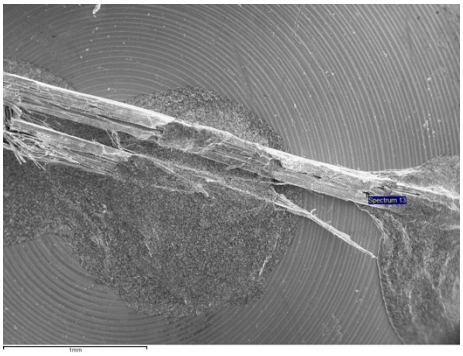

Figure 1: SEM image of the Rb2Mo6Se6 sample measured at Xmas.

At the Se K-edge we collected data at the following temperatures and angles:

$Rb_2Mo_6Se_6$.- temperatures: 4K, 75K, 100K, 150K (missing two highest angles), 295K.
angles: 0 °, 10 °, 30 °, 50 °, 70 °, 90 °, 110°.

$Tl_2Mo_6Se_6$.- temperatures: 4K, 8K, 75K, 100K, 150K, 295K.
angles: 0 °, 10 °, 30 °, 50 °, 70 °, 90 °.

Results: overall, we can say the experiment was successful. Detailed analysis is ongoing but a preliminary screening of the data show a structural distortion in the $Rb_2Mo_6Se_6$ EXAFS data (see Fig. 2), hence confirming that there is a change in the local structure that might potentially be linked to the metal-insulator transition. We are in the process of modelling the data to identify which atomic positions are responsible for this change in the signal. There is no evidence of a similar transition in the $Tl_2Mo_6Se_6$, which again supports the link between the distortion and the turn in the conductivity data for the Rb sample. The effect is most evident for the measurements with the polarisation in the *ab*-plane and parallel to *c* (only one showed due to space limitations).

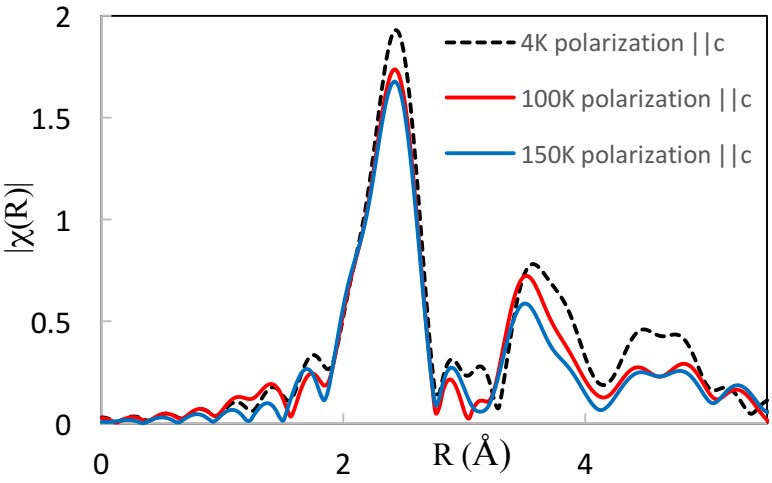

Figure 2: EXAFS data as a function of R for $Rb_2Mo_6Se_6$ at three different temperatures. Note that at the lowest temperature the peak at ~ 3.5 Å is broader, with a more intense shoulder that can only be explained by a distortion in the structure.

We will be presenting these results at SCES17 (abstract accepted for a poster) and intend to publish the results in the near future.