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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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:** X-ray and Raman study under pressure of the Mott insulators GaM_4Se_8 (M=Nb, Ta) : unravelling a Mott transition, and a possible spin gap / superconducting phases coexistence	**Experiment number**: HS-4200
Beamline:	**Date of experiment**: from: 03/11/2010 to: 09/11/2010	**Date of report**: *Received at ESRF:*
Shifts:	**Local contact(s)**: Michael Hanfland	

Names and affiliations of applicants (* indicates experimentalists):

Laurent Cario*, Institut des Matériaux Jean Rouxel (Nantes, France)
Benoît Corraze*, Institut des Matériaux Jean Rouxel (Nantes, France)
Vincent Guiot*, Institut des Matériaux Jean Rouxel (Nantes, France)
Etienne Janod*, Institut des Matériaux Jean Rouxel (Nantes, France)
Gaston Garbarino*, ESRF

This experiment carried out at ID09 aimed to establish the temperature-pressure phase diagram of the Mott insulators GaM_4Se_8 (M= Nb, Ta), which are rare examples of inorganic compounds that undergoes metal-insulator-superconductor transitions under pressure. X-Ray diffraction under pressure should allow to clarify the existence and position of three transition lines :
(1) the new structural transition line observed at very high pressure ($p_S \approx 26$ GPa) in our preliminary measurement at 300 K,
(2) the first order transition line expected at the Mott transition under pressure,
(3) the spin gap phase transition line which exists below 52 K in $GaTa_4Se_8$ at ambient pressure.

(1) Transition towards the high pressure phase (HPP)
We were able to detect the existence of the HPP phase by scaning pressure at several temperatures. Fig. 1 that a structural phase transition occurs above $P_C(295K) \approx 22$ GPa in $GaTa_4Se_8$ at 295 K. This phase transition shifts to lower pressure ($P_C(73K) \approx 17$ GPa) at low temperature. The same transition also appears in $GaNb_4Se_8$ at a slightly lower pressure ($P_C(295K) \approx 17$ Gpa). In both compounds, this transition shows a large hysteresis : upon decreasing pressure, significant amounts of HPP phase can be still detected at 9 GPa in $GaNb_4Se_8$ at 295 K.

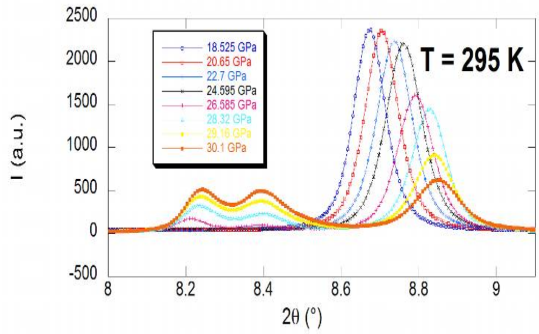

Fig.1 : phase transition from the ambient pressure $F\overline{4}3m$ phase towards the HPP phase in GaTa4Se8 at 295 K

(2) Mott transition
Theoretically, the typical fingerprints of a Mott metal-insulator transition under pressure are :
(i) the Mott insulator and metallic phases should be isostructural,
(ii) a volume collapse is expected going from the Mott insulating to the metallic phase.

It is already known from a transport study of $GaTa_4Se_8$ that the metal-insulator occurs between 5.5 and 8.4 GPa above 200 K[1]. Our study clearly shows that XRD data can be refined with the same $F\overline{4}3m$ space group below 5.5 GPa and above 8.4 GPa. Also, Fig. 2-a shows that the evolution of the cell parameter *a* as a function of the applied pressure can be nicely described with a Murnaghan Equation of State (EoS), *i.e.*

[1] M.M. Abd-Elmeguid *et al.*, Phys. Rev. Lett. **93**, 126403 (2004)

$a = a_0(\frac{K'}{K_0}p+1)^{\frac{-1}{3K'}}$. A clear deviation from this law appears at the transition towards the HP phase above 22 GPa. In order to detect a possible small drop of the unit cell *a*, we subtracted the smooth fitted Murnaghan dependance $a_{Murnaghan}(P)$ from the measured *a(P)*. Fig. 2-b shows that a very small drop of the cell parameter occurs at P_{Mott}(295K) = 6.5 ± 1 GPa. The Mott transition line poorly depends on temperature, since P_{Mott}(37K) = 6 ± 1 GPa (see Fig. 2-c). Noteworthy the volume contraction related to the Mott insulator to metal transition is very small in $GaTa_4Se_8$, $\Delta V/V \approx 0.1$ %, as compared *e.g.* with 1.2 % in V_2O_3 [2].

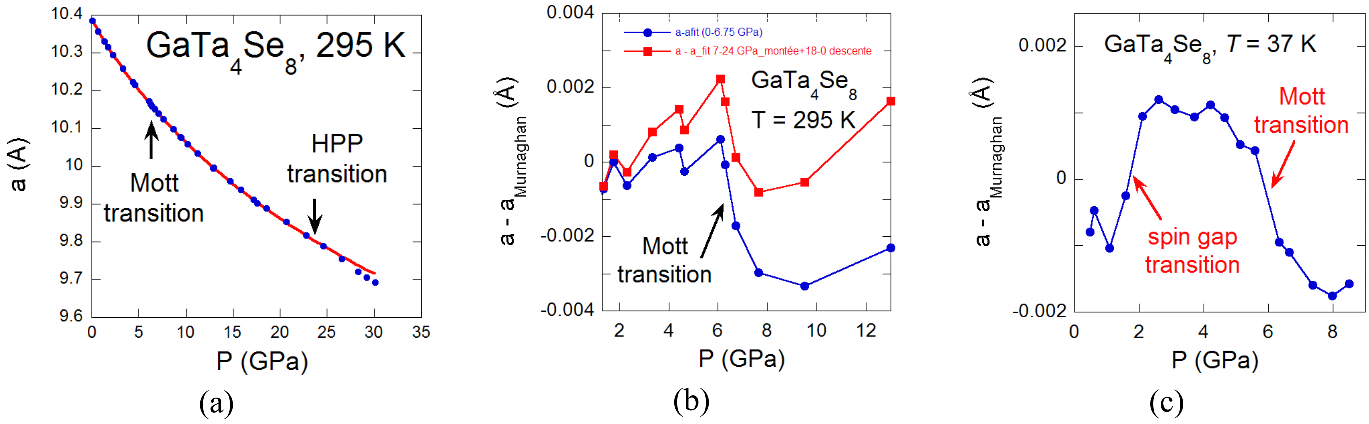

Fig. 2 : (a) pressure dependence of the cell parameter of $GaTa_4Se_8$ at room temperature, fitted using a Murnaghan EoS. (b and c) difference between the measured and fitted cell parameter *a vs.* pressure at 295 K (b) and 37 K (c) in $GaTa_4Se_8$.

(3) spin gap phase transition

By decreasing temperature below the spin gap temperature ($T_{spin\ gap}$ = 52 K), we observed the appearance of very weak super-structure peaks (see Fig.3). These new peaks corresponds to a change from a *F* to a *P* centering, in agreement with our recent low temperature XRD study of $GaTa_4Se_8$ at ambient pressure. These new peaks tend to disappear with applied pressure. A precise determination of $P_{spin\ gap}$(37 K) is difficult using these data only. However we note that a relative volume increase ($\Delta V/V \approx 0.07$ %) occurs around 2 GPa (see Fig. 2c) at the same temperature. We have already observed a comparable volume change at the temperature-induced spin gap transition.

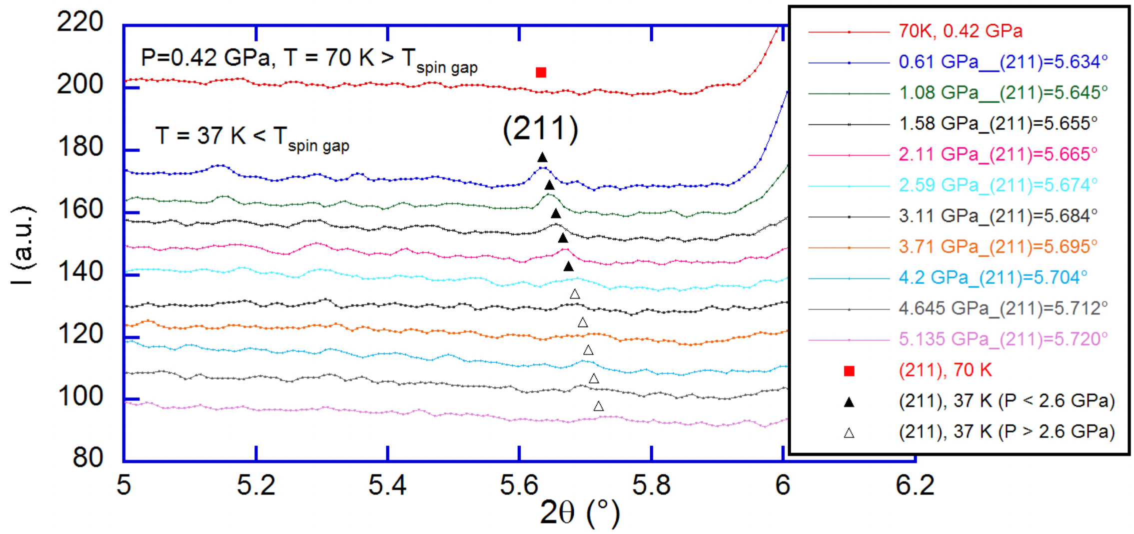

Fig.3 : zoom on the X-Ray diffraction patterns around the (211) peak in $GaTa_4Se_8$, forbidden in the high temperature $F\bar{4}3m$ phase but allowed in the *P*-centered spin gap phase. As expected, the (211) peak is absent at 70K, above the spin gap transition temperature $T_{spin\ gap}$ = 52 K at ambient pressure. Conversely, the peak appears at 37 K below $T_{spin\ gap}$ but progressively disappears by applying pressure.

Overall, these experiment were rather successful. New measurements at temperature lower than 37 K (around 5K) and on single crystals will allow to clarify the last unsolved part of the GaTa4Se8 temperature - pressure phase diagram

[2] D. B. McWhan, J.P. Remeika, Phys. Rev. B **2**, 3734 (1970)