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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 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: Equation of states and structural phase transitions of intermetallic compounds by angle dispersive X-ray powder diffraction at high .....**	**Experiment number**: CH995
Beamline: ID 09	**Date of experiment**: from: 04. Oct. 00 to: 08. Oct. 00	**Date of report**: 1. Sept. 03
Shifts: 12	**Local contact(s)**:M. Hanfland	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

A total of four publications have been finalized and submitted with the data having been measured during the experiment at the ESRF. They are accepted and printed. Please find attached the abstracts.

Pressure-induced Change of the Oxidation State of Ytterbium in $YbGa_2$

U. Schwarz [a,*], R. Giedigkeit [a], R. Niewa [a], M. Schmidt [a], W. Schnelle [a], R. Cardoso [a], M. Hanfland [b], Z. Hu [c], K. Klementiev [d], and Yu. Grin [a]

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Abstract. The crystal structure and the electronic properties of $YbGa_2$ realising a $CaIn_2$ type atomic arrangement were characterised at ambient conditions using single crystal X-ray diffraction data and magnetic susceptibility measurements at ambient pressure. Pressure-induced changes of structural and electronic properties of $YbGa_2$ were measured by means of angle-dispersive X-ray powder diffraction and XANES at the Yb L_{III} threshold. At pressures above 22(2) GPa, $YbGa_2$ undergoes a structural phase transition into a high pressure modification with a UHg_2 type crystal structure. Parallel to the pressure-induced structural alterations, ytterbium in $YbGa_2$ undergoes an increase of the oxidation state from +2 at ambient conditions to +3 in the high-pressure phase. Quantum chemical calculations of the Electron-Localisation-Function confirm that the phase transition is associated with a conversion of the three-dimensional gallium network of the low-pressure crystal structure into two-dimensional gallium layers in the high-pressure modification.

Pressure-induced Changes of the Crystal Structure of Eu_4P_3

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Abstract. Pressure-induced structural changes and electronic properties of rhombohedral Eu_4P_3 were characterised by means of angle-dispersive X-ray powder diffraction and X-ray absorption spectroscopy at the Eu L_{III} threshold. The measurements at low pressures indicate oxidation states of the europium atoms which are compatible with a composition $Eu_3^{2+}Eu^{3+}P_3$. At a pressures of 8(1) GPa, Eu_4P_3 undergoes a structural phase transition into a cubic high pressure modification with a Th_3P_4 type crystal structure thereby perpetuating the character of a compound with a non-integer oxidation state of the europium atoms.

Chemical Bonding and Pressure-Induced Change of the Electron Configuration of Ytterbium in β-$YbAgGa_2$

Ulrich Schwarz [a,*], Marcus Schmidt [a], Roman Gumeniuk [a,d], Walter Schnelle [a], Michael Hanfland [c], Konstantin Klementiev [b], and Yuri Grin [a]

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Abstract. The single-phase polycrystalline intermetallic compound β-$YbAgGa_2$ was synthesized by inductive heating and subsequent annealing for eight weeks at 670 K. Magnetic properties were characterized by susceptibility measurements and indicated intermediate valence of ytterbium at ambient pressure. Angle-dispersive X-ray powder diffraction data of orthorhombic β-$YbAgGa_2$ indicate stability of the phase in the investigated pressure range from 0.1 MPa (ambient pressure) to 19 GPa. The pressure-induced volume decrease is accompanied by an increase of the effective valence from 2.17 at ambient conditions to 2.71 at 16 GPa as evaluated by X-ray absorption spectroscopy at the Yb L_{III} threshold. Analysis of the chemical bonding in β-$YbAgGa_2$ by integrating the electron density of the polyanion in basins as defined by the electron localization function results in an electron count $Yb^{2.7+}[(Ag^{0.2-})(Ga1(3b)^{1.0-})(Ga2(4b)^{1.5-})]$. This finding is close to the expected values calculated by means of the Zintl rules and fits the results of magnetic susceptibility measurements and XAS investigations well.

Crystal Structure and Properties of $Yb_{1+x}Mg_{1-x}Ga_4$ (x = 0.05) and $YLiGa_4$ with a new superstructure of the $CaIn_2$ type

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Abstract. The compounds $Yb_{1+x}Mg_{1-x}Ga_4$ (x = 0.05) and $YLiGa_4$ were synthesised by reaction of the elements in sealed niobium crucibles. The atomic arrangement of $Yb_{1.05}Mg_{0.95}Ga_4$ represents a new structure type (SG $P\bar{6}m2$, a = 439.34(2) pm and c = 695.78(6) pm) as evidenced by single crystal structure analysis and can be described as an ordered variant of $CaIn_2$. $YLiGa_4$ is isotypic as evidenced by Guinier powder data. Measurements of the magnetic susceptibility of both compounds reveal intrinsic diamagnetic behaviour, i.e., for $Yb_{1.05}Mg_{0.95}Ga_4$ ytterbium in the $4f^{14}$ configuration. From electrical resistivity data both compounds can be classified as metals. The X-ray absorption spectra of the Yb L_{III} edge of $Yb_{1.05}Mg_{0.95}Ga_4$ at pressures between ambient and 25.0 GPa show a two-peak structure which reveals the presence of Yb in the $4f^{14}$ (Yb^{2+}) and $4f^{13}$ (Yb^{3+}) states. The amount of $4f^{13}$ (Yb^{3+}) increases with progressing compression. The change of the electron configuration is reflected by a pronounced compressibility.

References:

U. Schwarz, R. Giedigkeit, R. Niewa, M. Schmidt, W. Schnelle, R. Cardoso, M. Hanfland, Z. Hu, K. Klementiev, Yu. Grin, *Pressure-induced oxidation state change of ytterbium in $YbGa_2$,* Z. Anorg. Allg. Chem. **627**, 2249 (2001).

R. Cardoso-Gil, R. Niewa, M. Schmidt, M. Armbrüster, M. Hanfland, K. Klementiev, U. Schwarz, *Pressure-induced changes of the crystal structure of Eu_4P_3,* Z. Anorg. Allg. Chem. **629,** 454 (2003)

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