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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

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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:** Structural Study of Samarium at High Pressure	**Experiment number**: HC 805
Beamline: ID09a	**Date of experiment**: from: 13/04/13 to: 16/04/13	**Date of report**:
Shifts: 9	**Local contact(s)**: Lucile Bezacier	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

R. J. Husband*, I. Loa*, K. Munro*, G.W. Stinton, E. E. McBride and M. I. McMahon.

SUPA, School of Physics and Astronomy and Centre for Science at Extreme Conditions, The University of Edinburgh

Report:

The trivalent lanthanide elements are known to exhibit a common series of close-packed structures under pressure (hcp → Sm-type → dhcp → fcc), transforming to a distorted-fcc (dfcc) phase on further compression. The high-pressure structural behaviour of these elements is therefore often thought to be well known. However, structural assignment of the dfcc phase must be performed with care, as different distorted-fcc structures can give very similar diffraction patterns. Evans *et al*. [1] determined the dfcc phase of Pr to have a rhombohedral *hR*24 structure, but the monoclinic *mC*4 structure could only be ruled out due to the observation of a small number of very weak reflections. The same authors also reported Pr to undergo a transition to a second distorted-fcc structure, *oI*16, on further compression. The dfcc phases of the majority of the remaining trivalent lanthanides have been reported to have the same *hR*24 structure as in Pr, but these assignments have relied heavily on analogy with Pr. However, in addition to Pr, the transition to a second dfcc phase has only been observed in Nd [1]. Sm transforms to the dfcc phase above 20 GPa [2], but the structure has not yet been definatively determined, and instead it has been indexed as either trigonal (*hP*6) [3], or *hP*6 at lower pressures and monoclinic at higher pressure [2].

We were awarded 3 days on ID09a (experiment HC-805) to study the high presure structures of Sm, with the aim of making a comparison with neighbouring divalent Eu and trivalent Pr. Three Sm samples were compressed to a maximum pressure of ~55 GPa, and data were collected in 2-3 GPa steps in order to carefully pin down transition pressures.

In all our samples we observed the low-pressure phases in agreement with previous studies. However, although we observed mixed-phase dhcp/fcc patterns, we did not observe any single-phase fcc patterns on pressure increase, and instead the first dfcc pattern was collected at 18.7 GPa. The integrated diffraction profiles from the dfcc phase were extremely sharp, and we were able to resolve the splitting of the high-angle dfcc reflections even at the lowest pressure. The splitting of low-angle reflections could also be resolved at higher pressures. The *hR*24 structure gave an excellent fit to the dfcc patterns over the entire pressure range in which this phase was observed, and the reflections that rule out the *mC*4 structure were present in all patterns. In Pr, the subtle transition to the second dfcc phase was identified by the change in the relative intensity of the (006)/(202) and (0,0,12)/(404) reflections, which was identified as the disappearance of the (006) and (0,0,12)-*hR*24 reflections and the growth of new reflections from the *oI*16 phase with very similar *d*-spacings. The pressure-dependence of the (006)/(202) and (0,0,12)/(404) reflections in Sm is shown in insets (a) and

(b) of Figure 2. It is clear from this figure that no new reflections appear with increasing pressure, and Sm thus remains in the *hR*24 phase for the entire pressure range.

On compression, the splitting of the fcc reflections increases with increasing pressure. Correspondingly, the *c/a* ratio increases continuously from 2.463(7) at 18.7 GPa, reaching a maximum value of 2.507(8) at 42.6 GPa, as shown in Figure 2. This is significantly larger than the maximum value of 2.487 reported for *hR*24-Pr by Evans *et al.*

On further compression, we observed a sluggish transition to the *hP*3 phase at ??? GPa, in agreement with previous studies [4]. Sm remained in this phase up to 55 GPa, the highest pressure reached in this study.

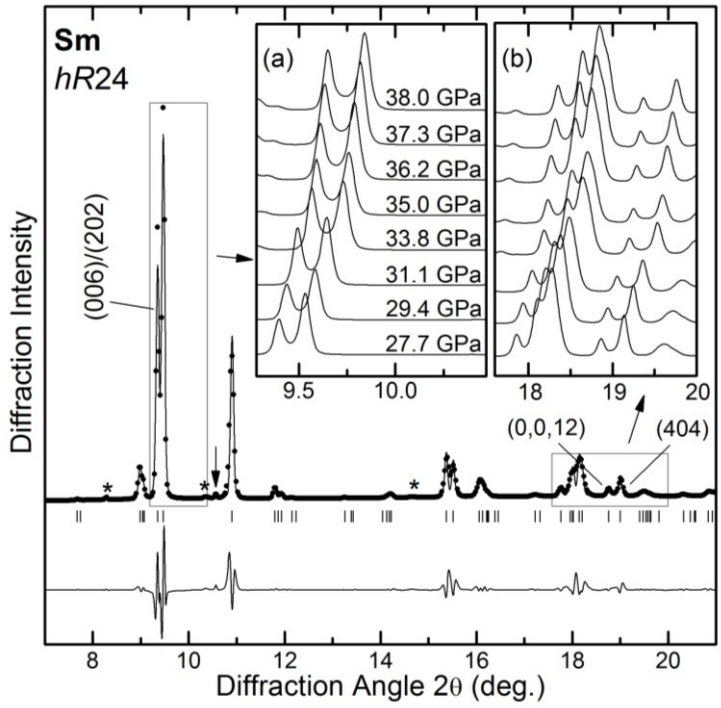

Fig. 1 Rietveld refinement of the *hR*24 structure based on the diffraction profile of Sm at 29.3 GPa. The insets show the evolution of the (a) (006) and (202) and (b) (0,0,12) and (404) reflections on pressure increase. The asterisks indicate reflections from two contaminant phases, and the arrow indictes the reflection from the Ta pressure marker.

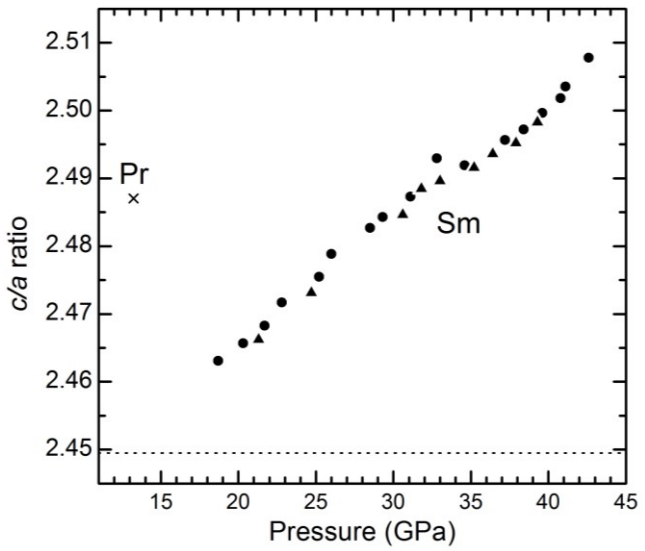

Fig. 2. Pressure dependence of the *c/a* ratio of *hR*24-Sm. The dotted line indicates the value of undistorted fcc (√6). The cross shows the maximum *c/a* ratio for *hR*24-Pr reported by Evans *et al*.[1]

In conclusion, we have determined the dfcc phase of Sm to have the same *hR*24 structure observed in Pr. However, Sm does not transform to a second dfcc phase such as the *oI*16 structure observed in Pr, and instead the *hR*24 structure distorts to a greater extent. On further compression, Sm transforms to the *hP*3 phase in agreement with previous studies. The differences in the high-pressure structural behaviour of Sm and Pr illustrate that it is not sufficient to perform structural assignment based on analogy with other members of the lanthanide series. These elements are known to be difficult for electronic structure calculations, and these subtle structural differences provide a challenge for future studies looking at the high-pressure behaviour across the lanthanide series.

Details of this work were presented at the joint SCCM/AIRAPT conference in July 2013. A manuscript has been submitted as conference proceedings and is currently under review.

References

[1] Evans *et al.,* Phys. Rev. B **80** 13410 (2009).
[2] Olsen *et al.*, High Pressure Res. **4** 366-368 (1990).
[3] Krüger *et al.,* High Pressure Res. **2** 193 (1990).
[4] Zhao *et al.,* Phys. Rev. B **50** 6603 (1994).