ESRF	**Experiment title:** **Structures and Transitions in Europium to 150 GPa**	**Experiment number:** HS-4186
Beamline: ID09a	**Date of experiment:** 19 Feb 2011 – 21 Feb 2011 & 20 July 2011	**Date of report:** 15/04/12 *Received at ESRF:*
Shifts: 9	**Local contact(s):** S. Evans	

Names and affiliations of applicants (* indicates experimentalists):

M.I. McMahon* School of Physics & Astronomy and Centre for Science at Extreme Conditions
R. J. Husband* The University of Edinburgh
I. Loa* Edinburgh, U.K.
G. Stinton* & E. McBride*

Europium (Eu) and Ytterbium (Yb), as a result of their half filled and full 4f electron shells, respectively, are unique in being the only divalent members of the lanthanide series, in contrast with the remaining elements which are trivalent. As a result, both Eu and Yb have significantly larger atomic volumes at ambient pressure, and larger compressibilities, than would be expected to be in keeping with the general trends observed across the lanthanide series [1]. Initial spectroscopic studies found that under pressure, Eu undergoes a continuous transition to a mixed valence state, with the valence increasing from 2.03 at ambient pressure to 2.64 at 18 GPa. However, very recent work has reported that Eu remains nearly divalent up to 87 GPa [2]. Eu was also recently found to become a superconductor above 80 GPa [3], with the lowest critical temperature of all the superconducting lanthanide elements [4].

Initial diffraction studies reported that Eu transforms from the ambient-pressure body-centred cubic (*bcc*) structure to the hexagonal close-packed (*hcp*) structure at 12.5 GPa [1,5] before transforming to Eu-III at 18 GPa. The structure of Eu-III has long resisted solution, and there were no reported diffraction studies of Eu for over two decades until Bi *et al.,* prompted by the discovery of superconductivity, reported x-ray diffraction results up to 92 GPa [6].

We were awarded 3 days of beamtime on ID09 to study the structural behaviour of Eu up to 150 GPa. We studied a number of samples to a maximum pressure of 70 GPa, loaded in both helium and with no pressure-transmitting medium. In our initial samples we identified the presence of two contaminant phases with rhombohedral and cubic structures, one of which produced all of the diffraction peaks previously attributed to Eu-III. Detailed results of these contaminant phases are to be published in the conference proceedings for the International Conference on High Pressure Science and Technology (AIRAPT) 2011. This introduces the problem of misidentification of contamination peaks as those from pure Eu in previous studies. As a result, we found that <u>none</u> of our data above 18 GPa could be described by the structures proposed by Bi *et al*. The results from our three days of beamtime thus overturned 25 years of previous diffraction work on Eu, and for this reason we limited the upper pressure of this study to 70 GPa to focus on the previously-misidentified lower-pressure phase transitions.

In order to reduce possible sources of contamination, subsequent Eu samples were loaded without any pressure-transmitting medium and without any pressure calibrant in the ESRF glovebox. In these samples, we did not observe the additional reflections at 18 GPa, and Eu remained in the *hcp* phase up to 32 GPa. This confirmed that the patterns previously attributed to Eu-III were in fact *entirely* due to pressureinduced changes in a contamination phase, and not due to a structural transition in pure Eu. A comparison of a diffraction profile from pure Eu, and that of Eu plus the rhombohedral contamination phase at the same pressure, is shown in figure 1.

We were then able to identify two new phase transitions at 31 GPa and 38 GPa. Increasing the sample-to-detector distance to 500 mm in the July 2011 beamtime enabled us to resolve the splitting of many of the reflections into closely-spaced doublets or triplets above 32 GPa, which had not been observed in previous studies, including those we made in the February 2011 beamtime. The phase above 32 GPa was then solved as having an incommensurately-modulated monoclinic structure – the first incommensurate structure ever observed in the lanthanide elements. It is also the first incommensurately-modulated structure with a two-dimensional modulation vector to be observed in the elements at high pressure. A Rietveld refinement of this structure at 33.9 GPa is shown in Figure 2. This work is about to be submitted to Physical Review Letters. The diffraction patterns observed above the 38 GPa transition are also complex, and the large number of weak reflections suggest the possibility of a transition to another incommensurately modulated structure. Analysis of this new phase is in progress.

Due to the observation of the two new phase transitions at 32 and 38 GPa in our non-contaminated samples, we made the decision to focus our experiment on collecting and interpreting data up to a maximum pressure of 70 GPa. Collecting data in the higher pressure region will form the basis of a new proposal to ID09a.

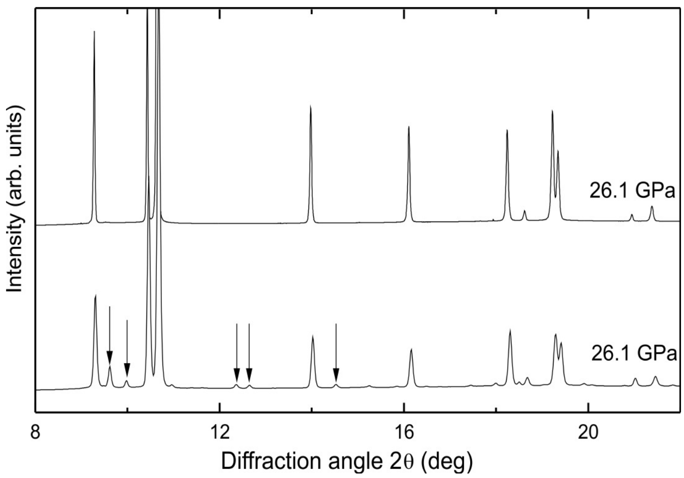

Figure 1: The diffraction profile of *hcp*-Eu plus the rhombohedral contaminant (lower) and pure *hcp*-Eu (upper) at the same pressure of 26.1 GPa. The tick marks show the positions of the most intense new reflections in Eu-III that were reported in the initial study by Takemura and Syssen [1].

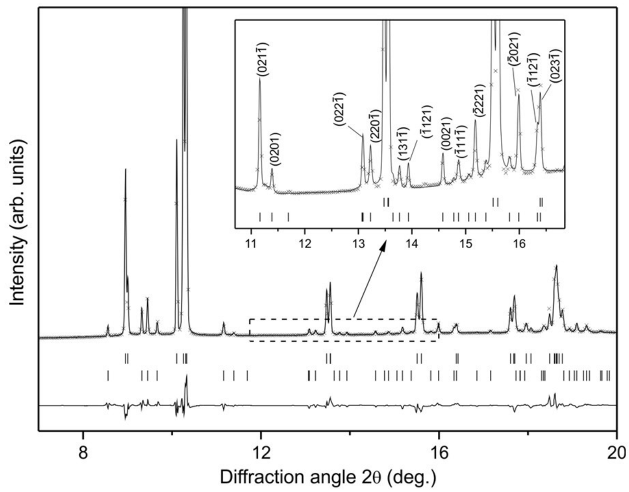

Figure 2: Rietveld refinement of the incommensurate structure to the diffraction profile of Eu at 33.9 GPa taken in this experiment. The tick marks show the calculated peak positions of the main (upper) and satellite (lower) reflections. The residuals are shown below the tick marks. The inset shows the excellent fit to the large number of additional weak satellite reflections.

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[3] Bi *et al.* arXiv:1203.3387v1
[4] Debessai *et al*, Phys. Rev. Lett. **102**, 197002 (2009).
[5] Krüger *et al*, High Press. Res. **2,** 193 (1990).
[6] Bi *et al*, Phys. Rev. B. **83**, 104106 (2011).