



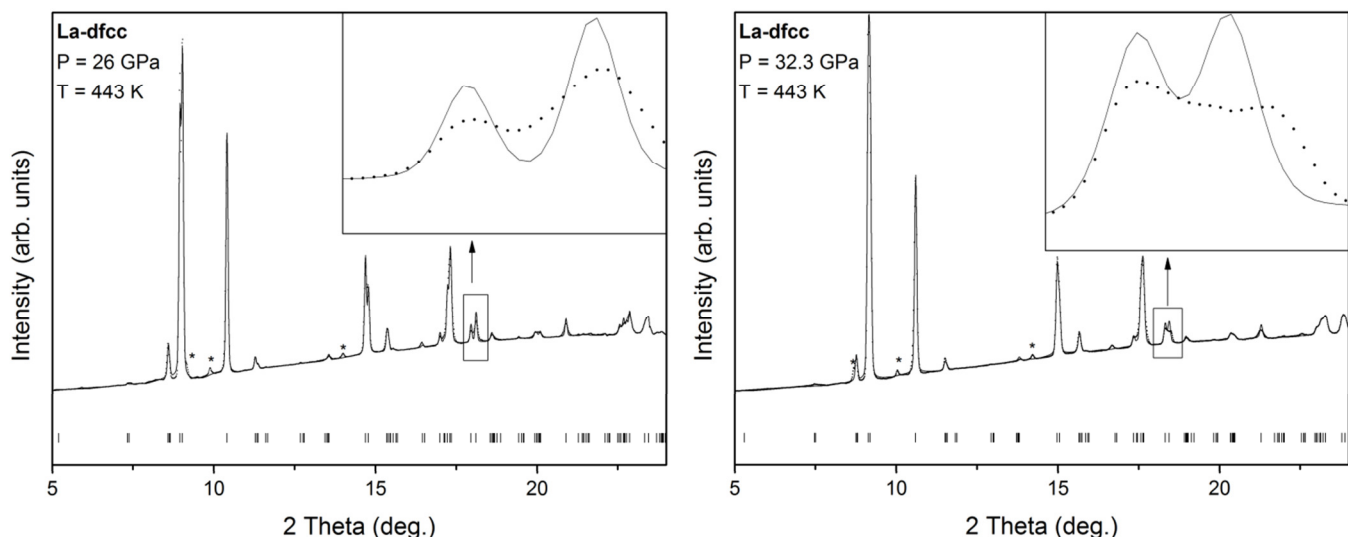
<b>Beamline:</b> ID09a	<b>Experiment title:</b> Diffraction Study of the High Pressure Distorted-FCC Phases of Lanthanum Metal	<b>Experiment number:</b> HC-1338
	<b>Date of experiment:</b> from: 09 Apr 2014 to: 12 April 2014	<b>Date of report:</b> 10/08/2014
	<b>Shifts:</b> 9	<b>Local contact(s):</b> LucileBezacier and Michael Hanfland
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## Report:

The trivalent lanthanide elements are known to adopt a series of close-packed structures under pressure (hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc  $\rightarrow$  distorted-fcc (d-fcc)  $\rightarrow$  “volume collapsed” phase). The behaviour of these elements is thought to be well known, yet there have been many structures assigned to the d-fcc phase. It was only recently that Evans *et al.* [1] confirmed the d-fcc phase of praseodymium to have the *hR24* structure, which was first proposed by Hamaya *et al.* [2], rather than other, lower-symmetry structures reported by others [3]. The assignment of the *hR24* structure to the d-fcc phase of praseodymium, rather than the monoclinic *mC4* structure, was only possible due to the observation of very weak peaks in the integrated diffraction patterns. The d-fcc phases of many of the other lanthanide metals have also been reported to have the *hR24* structure, but these assignments rely heavily on analogy with praseodymium. Evans *et al.* also reported a transformation to a new structure (*oI16*) in praseodymium **before** the transition to the “volume collapsed” phase. This *oI16* structure has also been observed in neodymium and is characterized by subtle changes in the *hR24* diffraction pattern. Preliminary data collected by us at Diamond suggested that a transition to the *oI16* structure also occurs in lanthanum, which is unique amongst the lanthanide metals in not having any electrons in the 4*f* electron shell at ambient conditions. As a result, lanthanum deviates from the general lanthanide transformation sequence given above, and instead of undergoing the d-fcc  $\rightarrow$  “volume collapsed” phase transition, it undergoes a re-entrant transition at 67 GPa back into the fcc phase observed at lower pressures [4]. The phase boundary between the fcc and d-fcc phases has been partially mapped out by Sepiel *et al.* [5].

We were awarded 3 days of beamtime at ID09 to study the structural behaviour of lanthanum to 70 GPa. Three samples were compressed up to 60 GPa while simultaneously being heated, and data were collected in 2-3 GPa steps in order to pin down the transition pressures. No pressure medium was used in order to prevent any contamination of the sample. A grain of tantalum powder was used as the pressure marker.

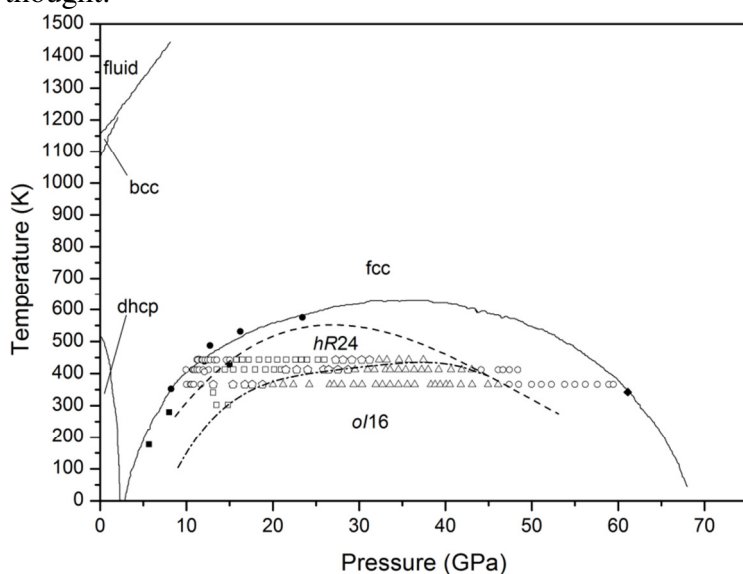
We observed the low-pressure phase transitions at slightly higher pressures compared to previous studies, although this might be due to the lack of a pressure medium. The d-fcc phase at pressures below 21.5 and 27.3 GPa at 412 and 443 K, respectively, do indeed have the *hR24* structure, and the reflections that rule out the *mC4* structure are present in all patterns. The rhombohedral splitting of peaks in the *hR24* pattern is much smaller than that we have seen in praseodymium, neodymium, samarium and terbium. At 366 K, the fcc phase transforms sluggishly directly into the *oI16* structure. We observe changes in the integrated diffraction patterns of lanthanum over several GPa, near 27 GPa at 443 K (see Figure 1), which are similar to those seen by Evans *et al.* during the *hR24*  $\rightarrow$  *oI16* transition in praseodymium and neodymium.



**Figure 1:** Rietveld refinements of d-fcc lanthanum at 26 and 32.3 GPa at 443 K. The asterisks mark peaks from an oxide contaminant. The inserts show enlargements of the (00,12)/(404) doublet. At 26 GPa, the splitting of the doublet is well accounted for by the *hR24* structure. However, at 32.3 GPa, a 3<sup>rd</sup> peak has emerged, which cannot be accounted for by the *hR24* structure.

It is not yet clear if the diffraction profiles obtained at 32 GPa can all be accounted for by this new phase, or are from a mixed phase of the *oI16* and *hR24* structures. Once the triplet shown in Figure 1 is formed, it persists until the sluggish transition back to the fcc phase starts at 40 and 35.4 GPa at 366 and 412 K, respectively, where the three peaks combine back into a single peak of the fcc phase.

We also explored the re-entrant phase transition at high temperature to further constrain the fcc/d-fcc phase boundary. At high pressures we see that the re-entrant transition back to the fcc phase occurs at a much lower pressure than has been predicted, which suggests that the phase boundary is different than previously thought.



**Figure 2:** The phase diagram of lanthanum to 70 GPa. The solid black data points show the location of the fcc → d-fcc transition from Seipel *et al.* The solid lines are phase boundaries from Seipel *et al.* The unfilled symbols show where data were collected in the present study: circles show where the fcc structure was observed, squares where we observed the *hR24* structure, the triangles where we found the *oI16* structure. The pentagons mark the sluggish *hR24* → *oI16* transition. The dashed lines are proposed phase boundaries based on the present study.

In conclusion, we can confirm that lanthanum undergoes a transformation at 13, 21.5 and 27.3 GPa at 366, 412 and 443 K respectively, similar to the *hR24* → *oI16* transformation seen previously by us in praseodymium and neodymium. However, it is not yet known if the complex diffraction patterns observed are from a single or mixed phase. The lanthanides are famously difficult for structure predictions and the subtle differences between the various structures are a challenge for future studies looking at high-pressure behaviour in the lanthanide series.

## References

- [1] Evans *et al.*, Phys. Rev. B **80**, 134105 (2009).
- [2] Hamaya *et al.*, J.Phys: Condensed Matter **5**, L369 (1993).
- [3] Dmitriev *et al.*, Phys. Rev. B **70**, 014104 (2004).
- [4] Porsch *et al.*, Phys. Rev. Lett. **70**, 4087-4089 (1993).
- [5] Seipel *et al.*, High Pressure Research **15**, 321-330 (1997).