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2014 J. Phys.: Conf. Ser. 500 032009
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The distorted-fcc phase of samarium

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Abstract. Angle-dispersive x-ray powder diffraction experiments were performed on samarium metal up to 50 GPa. We report that the high-pressure distorted-fcc phase has the same hR²⁴ structure observed in praseodymium, but, unlike praseodymium, samarium does not undergo a transition to a second distorted-fcc phase. We also report a path-dependent transition to a new phase, the structure of which has not yet been determined, which occurs on annealing followed by pressure decrease.

1. Introduction

The trivalent lanthanide elements exhibit a common series of structural phase transitions under pressure: hcp → Sm-type → dhcp → fcc → distorted-fcc (dfcc), which have long been associated with pressure-induced changes in their electronic structure. Due to this common structural trend, the structures of these high-pressure phases are often thought to be well known. However, the diffraction patterns generated by several distinct distorted-fcc structures can be very similar, and great care has to be taken in order to definitively determine the structure of these phases. Despite this fact, in many cases structural assignments were performed by analogy with other elements in the series. Previous work on praseodymium (Pr) has shown that this method is not sufficient. Evans et al. [1] showed that the dfcc phase of Pr has a rhombohedral structure with 24 atoms per hexagonal unit cell (hR²⁴ in Pearson notation), and that a C-centred monoclinic structure (mC⁴) could only be ruled out due to the observation of a small number of weak reflections. The same study also showed that Pr transforms from hR²⁴ to a second dfcc phase, a body-centred orthorhombic structure with space group Ibam and 16 atoms in the unit cell (oI¹⁶). This subtle transition was identified by the observation of a change in the relative intensity of the (006)/(202) and (0,0,12)/(404) doublets. This transition is also most likely observed in neodymium (Nd), raising the question of whether this transition may occur in all the trivalent lanthanide elements.

While it was possible to obtain very high quality diffraction data from the dfcc phase of Pr, this has not always been possible at the higher pressures required to access this phase in the other trivalent lanthanide elements. Although the dfcc phases of the majority of the trivalent lanthanides have been reported to have the same hR²⁴ structure observed in Pr [2], these assignments rely heavily on analogy with Pr, and Rietveld refinements have only been shown for erbium and gadolinium [3,4]. Samarium (Sm) transforms to the dfcc phase above 20 GPa [5], but its structure has not yet been definitively determined: it has been indexed as either trigonal (hP6) [6], or hP6 at lower pressures and monoclinic at higher pressure [5]. At 37(4) GPa, Sm transforms to a hexagonal structure (hP3) [7], which is also observed in ytterbium (Yb) above 91 GPa [8]. Significant anomalies in the equation of state of Sm...
were observed in the dfcc and $hP3$ phases compared to the common behaviour of the other trivalent lanthanides, and this has been taken as evidence for the onset of $4f$ electron delocalization [7].

In this paper, we report the results of our angle-dispersive powder x-ray diffraction experiments on Sm up to 50 GPa. We have found that the dfcc phase of Sm has the same $hR24$ structure observed in Pr. However, unlike Pr, Sm does not undergo a transition to a second dfcc phase, and instead the $hR24$ structure distorts to a much greater extent than in Pr. Above 40.4 GPa, Sm undergoes a sluggish transition to the $hP3$ phase in agreement with previous studies. In addition, we report the onset of a path-dependent structural phase transition, which is observed on annealing at 32 GPa followed by subsequent pressure decrease. This transition is characterised by large intensity changes in the diffraction profile, with some of the $hR24$ reflections disappearing completely. On further pressure decrease, the intensity changes reverse back to that of $hR24$ before annealing, suggesting that the intensity changes are not due to preferred orientation.

2. Experimental Methods

High-purity Sm samples, supplied by U. Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden, were loaded in diamond anvil pressure cells equipped with tungsten gaskets in a dry argon atmosphere (<1 ppm $O_2$ and <1 ppm $H_2O$). Two samples were loaded without a pressure-transmitting medium (PTM) and small amounts of Ta powder were included as a pressure marker. These samples subsequently will be referred to as samples 1 and 2. The pressure was determined using the calibration by Hanfland et al. [9]. A further sample was loaded with a mineral oil PTM for comparison. A small ruby sphere was included for pressure determination, and the pressure was determined using the standard ruby fluorescence method using the calibration by Mao et al. [10]. This sample will subsequently be referred to as sample 3.

Angle-dispersive x-ray powder diffraction data were collected at the European Synchrotron Radiation Facility (ESRF), Diamond Light Source (DLS) and the PETRA III synchrotron source at DESY. Data on samples 1 and 2 were collected at beamline ID09a at the ESRF using a beam of monochromatic x-rays of wavelength of 0.41352 Å, collimated to a diameter of 15 µm, and a Mar555 area detector. Some additional data on sample 1 were collected at beamline P02.2 at PETRA III using an x-ray beam of wavelength of 0.289818 Å and a diameter of ~2 µm, and data on sample 3 were collected at beamline I15 at DLS using an x-ray beam of wavelength of 0.4132 Å with a diameter of 30 µm. Data from DLS and PETRA were collected on Mar345 image plate detectors. In all cases, the 2-d diffraction images were integrated using Fit2D [11,12] and Rietveld refinements were performed using the Jana software [13].

Despite loading high-purity samples in a dry, oxygen-free atmosphere, trace amounts of contaminants were present, and reflections from these contaminant phases were observed in the data collected at the ID09a and I15. However, due to its very small beam size, P02.2 is excellent for avoiding small amounts of sample contaminant. The data collected at this beamline then enabled us to obtain non-contaminated diffraction profiles, enabling us to identify two contaminant phases, both with an fcc lattice. However, due to the short wavelength used at P02.2, the closely-spaced Sm reflections could not be fully resolved. For this reason, the unit cell dimensions and atomic positions were determined using the data collected at ID09a and I15, where a longer wavelength was used.

3. Results and Discussion

In all of our samples, we observe the Sm-type $\rightarrow$ dhcp transition in agreement with previous studies. Although mixed-phase dhcp-fcc patterns were observed, no single-phase fcc patterns were seen in any of our samples, and a single-phase dfcc pattern was first observed at 18.7 GPa. The dfcc phase could clearly be identified by the appearance of non-fcc superlattice reflections, and although the splitting of the lower-angle fcc reflections could not be resolved at 18.7 GPa, some of the higher-angle fcc reflections, such as the (222) reflection, were clearly split at this pressure. On further compression, the splitting of the fcc reflections increased, allowing the lower-angle split reflections also to be resolved.
The hR24 structure provides an excellent fit to the dfcc patterns over the entire pressure range in which this phase was observed (18.7-42.6 GPa), and the weak reflections that rule out the mC4 structure [1] were present in all patterns. A Rietveld refinement of the hR24 structure based on the diffraction profile of Sm obtained at 41.4 GPa is shown in figure 1. The refined structural parameters are \( a = 5.891(1) \text{ Å} \), \( c = 14.748(3) \text{ Å} \), with atoms at \((0,0,0.273(1))\) and \((0.509(2),-0.509(2),0.244(1))\). The \((104), (216)\) and \((1\overline{1}8)\) reflections that cannot be accounted for by the mC4 structure are identified in the inset, and the strongest reflections from the two impurity phases are indicated by the asterisks.

The transition from hR24 to oI16 in Pr can be identified by a gradual change in the relative intensity of the (006)/(202) doublet, and in the \((2h,2k,2l)\) equivalent, \((0,0,12)/(404)\), which result from the splitting of the (111) and (222) reflections in the fcc phase. These intensity changes arise from the disappearance of the (006) and \((0,0,12)\)-hR24 reflections, and the simultaneous growth of new reflections from the oI16 phase with very similar \(d\)-spacings. The identification of a potential similar transition in Sm is greatly simplified by the fact that the splitting of the (111) and (222)-fcc reflections is much greater than in Pr. Consequently, the (006) and \((0,0,12)\) can be clearly identified as two distinct reflections for almost the entire pressure range in which this phase is observed, and the appearance of any additional reflections would be easily noticeable. The pressure dependence of the (006)/(202) and \((0,0,12)/(404)\) reflections for hR24-Sm are shown in insets (a) and (b) of figure 2. It is clear from these figures that there is no sign of any new reflections up to the maximum pressure. We therefore conclude that there is no transition in Sm to the oI16 structure on pressure increase at ambient temperature, and instead Sm remains in the hR24 phase up to 42.6 GPa.

The hR24 structure is identical to fcc when \(c/a = \sqrt{6} \approx 2.449\) and the atoms located at \((0,0,z)\) and \((x,-x,z)\) have \(z_1 = \frac{1}{4}, x = \frac{1}{2}\), and \(z_2 = \frac{1}{4}\). The departure of the structural parameters from these values then quantifies the distortion of the structure from fcc. 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 3.
Krüger et al. [6] reported the pressure dependence of the c/a ratio of the dfcc phase for all the trivalent lanthanides up to Tb, although this phase was indexed using a trigonal structure in all cases. The c/a ratio of Sm was reported to reach a value of about 1.015×√(2.486), which is a significantly larger distortion than that reported for La, Gd and Tb, in which the distortion from fcc is almost negligible. The c/a ratios of Pr and Nd were reported to reach values similar to that of Sm. However, if the data points from these latter two elements that occur in the pressure regions after the transition to the oI16 structure are disregarded, the remaining points would suggest that the c/a distortion of these elements is similar to that of La, Gd, and Tb. Evans et al. [1] subsequently reported the c/a ratio of Pr to increase continuously from √ to a maximum value of 2.47 at 3.24 GPa. Comparison with our data therefore suggests that the hR24-Sm distorts to a much greater extent than hR24-Pr.

In accordance with the analysis of Pr performed by Hamaya et al. [14], and subsequently by Evans et al. [1], the displacement of the hR24 atomic positions from those in the fcc structure can be expressed by amplitudes of three static displacements, ε = x – ½, δ1 = z1 – ¼ and δ2 = z1 – ¼. The pressure dependence of ε, δ1 and -δ2 for all three samples is shown in figure 4. In sample 1, ε and δ2 have different values. However, in samples 2 and 3, ε ≈ δ2, suggesting that the effect observed in the sample 1 is most likely due to the correlation between the atomic coordinates and the preferred orientation correction in the Rietveld refinement.

We observed the hR24 → hP3 transition at slightly different pressures in each of the three samples. The transition is sluggish, and the onset of the transition can be identified by the observation of the (100)-hP3 reflection, which was first observed between 40.4 and 40.8 GPa. Additional hP3 reflections were not observed until 42.0-43.4 GPa, and single-phase hP3 patterns were first observed between 43.2 and 46.2 GPa. No correlation between the use of a PTM and the transition pressure was observed. The hP3 structure can account for all the reflections observed in our diffraction profiles. A Rietveld refinement of this structure based on a diffraction profile collected at 47.4 GPa is shown in figure 5. The corresponding refined structural parameters are a = 2.9717(3) Å, c = 6.879(3) Å, with atoms at (0,0.513(5),½). Sm remained in this phase up to 50 GPa, the highest pressure reached in this study.

An attempt was made to collect diffraction data from sample 1 on decompression. The hP3 → hR24 transition was observed, and the first single-phase dfcc pattern was observed at 40.1 GPa.
However, only one more data point was collected at 37.9 GPa before the pressure of the cell dropped to 22.2 GPa. The $hR_{24}$ structure gave an excellent fit to these patterns. Additional compression data from the same sample up to 32 GPa, the maximum pressure that could be reached after pressure cycling, were collected at beamline P02.2. The integrated diffraction profiles were in agreement with those collected previously.

This sample was then annealed at 100°C for 12 hours at 32 GPa. After annealing, the pressure of the sample had increased slightly to 32.4 GPa. Although the subsequent diffraction pattern could still be described by the $hR_{24}$ structure, there was a significant change in the relative intensity of many of the $hR_{24}$ reflections. This effect became more pronounced when the pressure on the cell was subsequently decreased, with the intensity of some reflections decreasing further until they had disappeared completely. However, on further decompression the intensity changes reversed and the diffraction profiles strongly resemble those taken before annealing. This is illustrated in figure 6, which shows the diffraction profiles observed (a) before annealing at 32 GPa, (b) after annealing at 32.4 GPa, and on subsequent pressure decrease to (c) 28.5 GPa and then (d) 27.7 GPa, which were collected in that order. The sample was annealed for 12 hours at 100°C between the collection of profiles (a) and (b). The tick marks below profile (a) show the calculated peak positions of $hR_{24}$.

Further work will be required in order to determine the origin of this transition. In particular, it is not clear whether it will be observed on decompression at ambient temperature, or if the new phase is only stable at high temperatures. Many distorted-fcc structures have extremely similar diffraction patterns, and so high-resolution diffraction data will be required in order to resolve any closely-spaced
doublets and triplets. Subsequent data will therefore be collected using a longer x-ray wavelength in order to maximise the angular resolution.

4. Conclusion
We have reported the results of our angle-dispersive powder x-ray diffraction experiments on samarium metal up to 50 GPa. We report that the high-pressure distorted-fcc phase has the same \( hR_{24} \) structure observed in Pr. However, Sm does not undergo a transition to a second distorted-fcc phase such as the \( oI_{16} \) phase observed in Pr, and instead \( hR_{24}-\text{Sm} \) distorts to a greater extent than \( hR_{24}-\text{Pr} \). We also report a path-dependent transition to a new phase, the structure of which has not yet been determined, which occurred on annealing followed by pressure decrease.

Acknowledgments
This work was supported by a research grant from the UK Engineering and Physical Sciences Research Council, and facilities were provided by the ESRF and DLS. We would like to thank L. Bezacier of ID09a (ESRF) and H. Wilhelm of I15 (DLS) for their support on the beamlines, and U. Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden for the providing the samarium samples. Portions of this research were carried out at the light source PETRA III at DESY, a member of the Helmholtz Association (HGF). We would like to thank H. P. Liermann and Z. Konopkova for assistance in using beamline P02.2.

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