

High Pressure Structures in the Trivalent Lanthanides

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The trivalent lanthanides have long been known to exhibit a series of phase transformations with increasing pressure: hcp → Sm-type → dhcp → fcc → dfcc (distorted-fcc) → “volume-collapsed”. These have long been ascribed to changes in electronic structure [1]. Beyond the dfcc phase, considerably more complicated, low-symmetry “collapsed” structures are seen, most commonly the *mC4* monoclinic structure with space group *C2/m*.

However, despite previous extensive study in many of the lanthanide elements, there is still a strong disagreement as to the true structures of the post-dfcc phases in a number of lanthanides (praseodymium (Pr), neodymium (Nd), samarium (Sm) and the heavy trivalent lanthanides). Previous structural assignment via powder X-ray diffraction for the heavy trivalent lanthanides, in particular gadolinium (Gd), terbium (Tb) and dysprosium (Dy), has depended upon the “analysis by analogy” approach, where structural determination at high pressures in these elements depends on the solutions obtained with higher-quality data in the lower-Z elements at lower pressures [2,3]. Currently, analysis on the post-dfcc phases of Gd, Tb and Dy made by our group shows that the high pressure systematics of the trivalent lanthanides is incorrect (see Figure 1).

In addition, new data we have obtained from Sm above 200 GPa reveal that while it is more like Nd than previously reported [4], it too has peaks unexplained by the *C2/m* structure. Furthermore, this draws into question whether or not other light trivalent lanthanides exhibit similar structural systematics as Sm, Nd and the high-Z lanthanides.

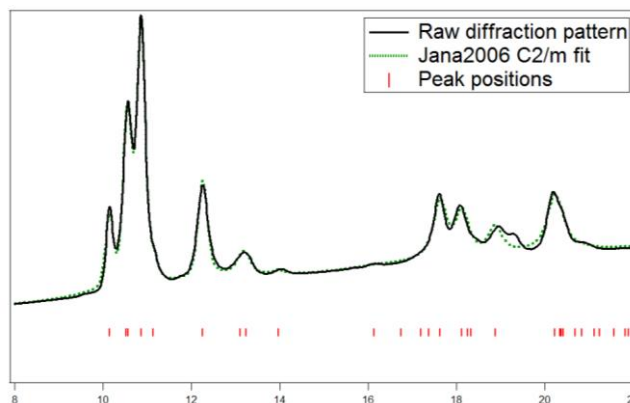


Figure 1. A LeBail refinement of the *C2/m* structure, reported in many other “collapsed” lanthanide phases, to our data collected from Dy at 75 GPa. While the fit is much better than that reported in the literature, the clear doublet at 20~19° is still unaccounted for, suggesting the structure is incorrect.

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