Static High Pressure Studies on Lanthanides Gd and Nd to One Megabar Pressure*

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The 4f lanthanide elements are important because they form a long series whose physical properties vary smoothly with 4f occupancy and thus allow detailed experimental and theoretical comparative studies. The lanthanide phase diagram can be fitted into a single universal phase diagram in which the same sequence of phase changes occurs either with decreasing atomic number or increasing pressure. This pattern has stimulated both theoretical and experimental studies on the lanthanides which have deepened our understanding of the group. Another important motivation for high pressure rare earth (4f) element research is the possibility that it provides a useful reference frame for the interpretation and understanding of the actinide (5f) elements.

In this report we present structural data for gadolinium up to 106 GPa (1.06 megabars) and neodymium to 80.0 GPa under static high pressure conditions and at room temperature.

Experimental

We used a diamond-anvil apparatus similar to that described by Mao and Bell [1]. In our experiments, we loaded gadolinium or neodymium samples together with small ruby chips (ten microns or less), a piece of copper (99.999% pure) and silicone oil into a 120 micron hole drilled into a T-301 stainless steel gasket that was preindented at 25 GPa pressure. The ruby chips and the piece of copper acted as the internal pressure calibrants, while silicone oil was the pressure transmitting medium. A rotating anode X-ray generator with Mo target was used for the X-ray source and the diffraction data were collected on film.

In our megabar experiments, however, the Gd sample and few grains of very fine ruby powder were loaded into a 100 micron gasket hole drilled into a similar stainless steel gasket that was also preindented to 25 GPa pressure. The diamonds used in this case were bevelled at a 7° angle and have a 400 micron culet with a 200 micron central flat face. X-ray diffraction data were obtained by an energy dispersive method at the National Synchrotron Light Source. The incident X-ray beam was collimated to widths of the order of 10–25 microns, and the diffracted X-ray beam was collected with a Si (Li) detector at ~18° 2θ scattering angle which was precalibrated at ambient pressure with a CeO_2 sample. Pressures were measured *in situ* by X-ray-induced ruby fluorescence [2].

Results

Up to a pressure of 106 GPa, gadolinium metal undergoes four structural transformations: h.c.p. → Sm-type → d.h.c.p. → f.c.c. → t.h.c.p. The corresponding transformation pressures are: 1.5 ± 0.2 GPa, 6.5 ± 0.5 GPa; onset at 24.0 GPa and completion at 29.0 GPa and between 44.0 GPa and 55.0 GPa, respectively. We found a much larger stability range for the f.c.c.-gadolinium phase than that reported by others. We tentatively indexed the post-f.c.c. phase as a triple hexagonal close-packed structure, which is a six-layered structure with an ABCACB repeat. On the assumption of a t.h.c.p. structure, at 106 GPa Gd has a $V/V_0 = 0.456$. The so-called collapsed structure for the rare earth elements [3] was not observed but may appear at still higher pressures.

Nd has the hexagonal close-packed (h.c.p.) structure under ambient conditions and transforms to a face-centered cubic (f.c.c.) structure at about 3.8 GPa. This pressure is slightly lower than the transformation pressure (5.0 GPa) reported by Piermarini and Weir [4]. At about 18.0 GPa we found new X-ray diffraction lines compared to the lower pressure f.c.c. phase. High pressure data between 18.0–38.0 GPa for Nd(III) were tested for a triple hexagonal close-packed (t.h.c.p.) structure, similar to that proposed for Pr(III) [5]. Nine out of twelve lines could be fitted to this structural form and three very weak lines ($I = 5$ to 10) could not be fitted. Lattice parameters for Nd(III) at ~18.0 GPa are $a = 3.262(18)$ Å, $c = 15.76(6)$ Å, $c/a = 4.831$ and $V/V_0 = 0.709$. There seems to be little volume contraction in going from f.c.c. to t.h.c.p. and the 30% volume compression observed at 18.0 GPa is similar to that of other rare earth elements.

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