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EQUATION OF STATE AND PHASE TRANSFORMATIONS STUDY OF Nd AT ULTRA-HIGH PRESSURES

J. Akella,[1] G. S. Smith,[1] J. Z. Hu,[2] and S. Weir[1]
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Neodymium was investigated to 96.0 GPa pressure in a diamond-anvil cell at room temperature. The observed structural sequence as a function of pressure is dhcp-fcc-"six layered" structure. In the diffraction pattern hexagonal doublets; notably 102, 006 and 110, 108; appear as single reflection when the c/a ratio is 4.899. However, when c/a approaches 4.7, the splitting is clear. So far in this study, no monoclinic phase or tetragonal phase were observed.

Keywords: Neodymium, diamond-anvil cell, phase changes, equation-of-state, high pressures.

INTRODUCTION

The 4f lanthanide elements form a long series whose physical properties vary smoothly as a function of f-band occupancy. Thus, a study of the systematics in the high pressure behavior of these elements is of theoretical and experimental importance. The suggested structural sequence for lanthanides as a function of pressure is hcp — Sm-type — dhcp — fcc (Jayaraman and Sherwood, [1]). This sequence of phase changes occurs either with decreasing atomic number or increasing pressure. Beyond the face-centered cubic structure, with increasing pressure, a "six-layered hexagonal" structure was discovered (Grosshans et al., [2] and Smith and Akella, [3]). At still higher pressures for Pr, an orthorhombic (α-U type) phase was reported (Smith and Akella [4], and Grosshans et al., [5]). Recently, Vohra et al., [6] have reported a body-centered tetragonal phase (bct) for Sm at about 90 GPa pressure which is similar to that in Ce (Endo et al., [7] and Olsen et al., [8]), and so far this phase is not reported in the other lanthanides.

Neodymium was studied previously by Piermarini and Weir [9], Grosshans [10] and Akella and Smith [11, 12]. In order to understand the post-fcc structural sequence for the light rare-earths, we have extended the high pressure investigation of Nd to 96.0 GPa, and the results are presented in this report.

EXPERIMENTAL PROCEDURE

The Nd samples were from a thin foil prepared by a sublimation process and is 99.9% pure. The sample was analyzed by optical emission spectroscopy. Minor amounts (<0.05 wt%) of some rare-earth impurities were detected.

We used a diamond-anvil cell (DAC) apparatus similar to that described by Mao and Bell [13]. Type 1A beveled diamond anvils with 150 μm central flat to a culet size of 300 μm and 7° bevel angle were used. The Nd sample, with Pt powder as a pressure marker, was loaded into the 75 μm-sample-hole drilled in a pre-indented, stainless-steel gasket. The sample and the marker act as their pressure medium.

Diffraction data were obtained at the National Synchrotron Light Source (NSLS) X-ray facility, hutch 17-C wiggler line. The X-ray spot from the synchrotron was collimated to ~10 μm diameter so that a small area of the sample could be X-rayed and the effects of large pressure gradients across the sample could be minimized. Energy dispersive diffraction (EDD) spectra were collected with an intrinsic germanium detector and the diffraction angle was calibrated by using a gold standard. Pressure was calculated from the measured lattice parameters of Pt in conjunction with the Pt equation-of-state to 660 GPa obtained by shock wave technique (Holmes et al., [14]). Measured pressures are accurate to ± 2 - 3 GPa at the highest pressure.

RESULTS AND DISCUSSION

Neodymium has a dhcp structure from room pressure up to 3.3 GPa and in the 4.5 GPa run very weak new reflections were observed. In the 6.9 GPa run the new high pressure reflections grew relative to the low pressure dhcp reflections. At 9.5 GPa we observed only fcc lines for Nd. The present data confirms Akella et al., [11] observations that Nd changes from dhcp to fcc structure at about 4.0 GPa. At 17.3 GPa pressure we saw clearly the splitting of Nd (111) reflection, and we assume that conversion to this new structural form could have occurred well above 12.6 and slightly lower than 17.3 GPa pressure. The new phase could be indexed to a "six layered hexagonal" structure (thcp, Smith and Akella [3], trigonal, Vohra et al., [15]). Formation of this "six-layered" structure was previously reported by Akella et al., [11] to be at about 18.0 GPa.

At 37.4 GPa and at still higher pressures, we observed a splitting in several of the hexagonal lines, notably the 102, 006 and 110, 108 doublets. In the ideal "six-layered" structure, the c/a ratio is $\sqrt{24}$ (= 4.899), and each of these doublets will appear as a single line in the diffraction pattern. These splittings we attribute to a decrease in the c/a ratio to a value of ~ 4.70. A similar occurrence was noticed previously in Gd by Akella et al. [16].

Grosshans [10] and Krüger et al [17] also reported a decrease in the c/a ratio with pressure for Nd, but only to the extent of ~1% at 37 GPa. These authors also reported that Nd has a monoclinic structure at about 41.0 GPa. This structural model requires, among other things, a splitting of the "six-layered" structure's 104 diffraction line into a medium and a strong line. However, in our diffraction runs above 41.0 GPa, we saw no such splitting of the 104 line, nor any major increase in intensity of this line. EDD spectrum at 42.8 GPa published by Krüger et al [17], in their report also does not show clearly such a splitting.

From our present study, we are not yet convinced that there is an orthorhombic or a monoclinic post-"six-layered" structure for Nd up to 90 GPa. We are pursuing an intense investigation above 35 GPa pressure to confirm or refute Grosshans' observation. Akella et al., [16] and Vohra et al., [6] also did not observe any overwhelming evidence for a post-"six-layered" orthorhombic or monoclinic structure in Gd up to 106 GPa and in Sm up to 90 GPa. The so called "collapsed" phase of Benedict et al.[18], is thus far seen unequivocally in Ce and Pr only, and only in Pr has a very large volume collapse been encountered.

We calculated the volume data for Nd at and above 17.3 GPa on the basis of a "six-layered" structure. In Fig. 1, volume compression (V/V_0) data for Nd are plotted as a function of pressure. Our data are compared with Grosshans' and our curve is 2-3% more compressible. We did not see any significant volume changes at the dhcp–fcc–"six-layered" phase transformation pressures. Body-centered tetragonal phase similar to that in Ce and Sm has not appeared in Nd so far.

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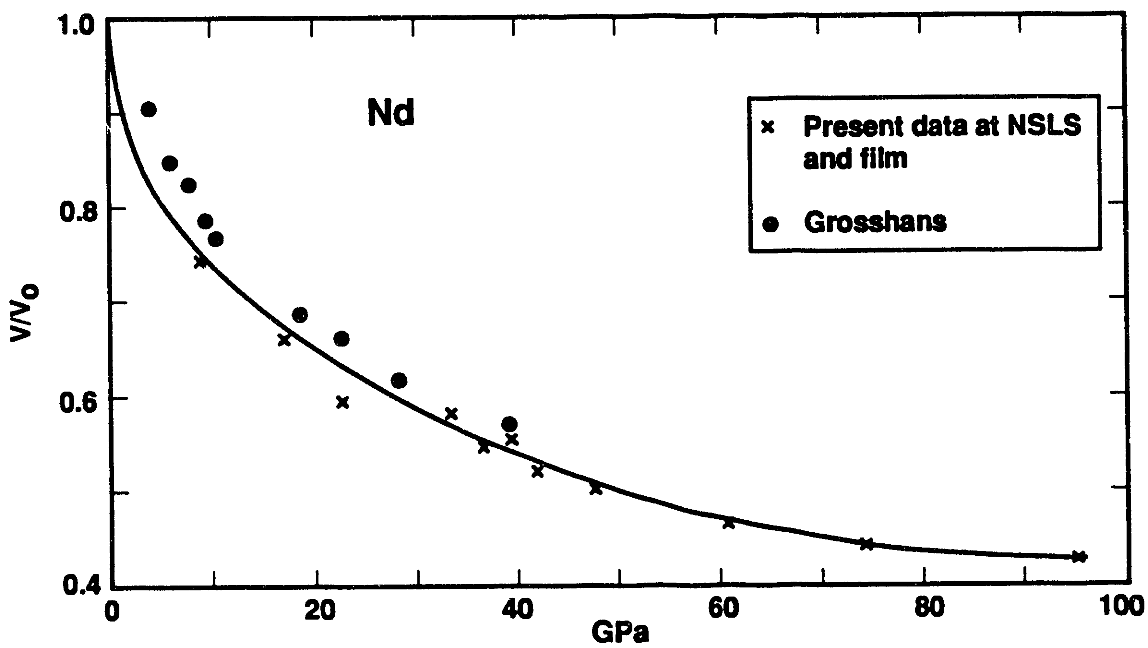

Figure 1. Pressure vs. volume (V/V_o) curve for Nd up to 90 GPa.

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