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## BRIEF REPORTS

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# Phase transformations and equation of state of praseodymium metal to 103 GPa

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Pressure-induced structural phase transformations in a trivalent rare-earth metal praseodymium (Pr) were studied at room temperature in a diamond anvil cell to 103 GPa by energy dispersive x-ray diffraction using a synchrotron source. Our x-ray diffraction studies document the following crystal structure sequence: dhcp→fcc→distorted fcc($hR24$ type)→monoclinic($C2/m$)→$\alpha$-uranium with increasing pressure. We measure a 16.7% volume collapse at the transition to the $\alpha$-uranium phase at 20 GPa. The high-pressure $\alpha$-uranium phase in Pr was found to be stable to the highest pressure of 103 GPa, which corresponds to a volume compression $V/V_0 = 0.407$.

Phase transformations in light rare-earth metals induced by pressure are of great interest because of the possibility of observing volume collapse transitions associated with the delocalization of the $4f$ shell or Mott transition in this class of metals.[1,2] A volume collapse accompanying this $4f$-shell delocalization is usually observed in light rare-earth metals cerium (Ce) at 0.7 GPa (Ref. 3) and in praseodymium (Pr) at 20 GPa.[4–6] However, the precise value of this volume collapse has not been clearly established in Pr as it depends on the precollapse crystal structures, which are not yet fully understood. The estimates have varied from 10% (Ref. 6) to 13% (Ref. 7) depending on the assigned precollapse crystal structures. It is widely accepted that after the volume collapse in the $\alpha$-uranium phase, $4f$ electrons are delocalized and contribute to bonding and cohesion in the metallic state at high pressures. Some $4f$ and $5f$ metals adopt a body-centered-tetragonal structure at high pressures[8] when the $f$ electrons are itinerant and behave like band electrons. An important issue to be considered is the eventual transition of Pr metal into a body-centered-tetragonal (bct) structure at ultrahigh pressures. In cerium, this transformation to bct structure occurs at 13 GPa,[9] and this transformation may occur in Pr metal at megabar pressures. Our present study on Pr metal is motivated by two considerations, first, to establish precollapse crystallographic phases below 20 GPa and, second, to investigate further phase transformations beyond the known $\alpha$-uranium phase to a possible bct phase at ultrahigh pressures.

Pr was studied in a diamond anvil cell at room temperature employing copper as an internal pressure marker. Two different experiments were carried out in our current study on Pr using energy dispersive x-ray diffraction with a synchrotron source. These different experiments ensure reproducibility of various transformations under varying conditions of sample thickness and pressure distributions. In both experiments we used spring steel for the gasket material. In the first experiment we employed diamonds with a central flat of 35 $\mu$m and a 7.5° bevel angle to a culet size of 350 $\mu$m in diameter, and a sample hole of 25 $\mu$m in diameter was filled with a polycrystalline sample of Pr and Cu. In the second experiment diamonds with a central flat of 100 $\mu$m and a 7° bevel angle to a culet size of 350 $\mu$m in diameter were employed and a sample hole of 50 $\mu$m in diameter was filled with Pr and Cu. For both experiments no liquid pressure medium was utilized since Pr is an extremely soft material and reactivity of Pr with alcohol and water pressure medium is a cause of concern. Energy dispersive x-ray diffraction data was recorded at $X17$-$C$ station at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The first x-ray diffraction experiment was performed with a microcollimated x-ray beam of $10\times10\,\mu\text{m}^2$ and the second experiment was performed with a beam size of $25\times25\,\mu\text{m}^2$. The x-ray diffraction data were collected both on increasing and decreasing pressure cycles and all transformations reported in this study were found to be completely reversible on decreasing pressure.

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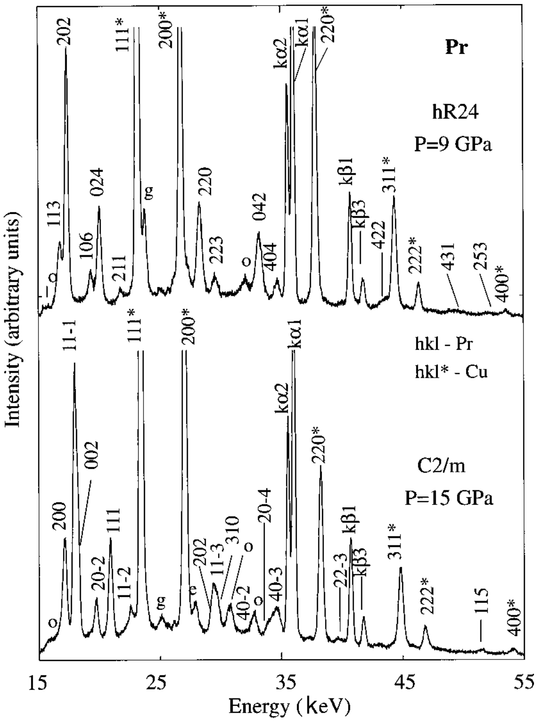

FIG. 1. Energy dispersive x-ray diffraction spectrums of Pr sample and copper pressure marker (peaks marked with an asterisk) at various pressures. $Ed = 47.461 \pm 0.008$ keV Å. The upper panel shows a pattern at 9 GPa indexed to a hexagonal phase ($hr24$) and the lower panel shows a spectrum at 15 GPa indexed to a monoclinic phase ($C2/m$, 4 atoms per cell). The weak peaks labeled *e, o*, and *g* correspond to an escape peak, oxide peak, and gasket peak, respectively.

TABLE I. The comparison of the observed and calculated interplanar spacing $d_{hkl}$ and the observed and calculated intensities for the x-ray diffraction data for praseodymium at 15 GPa. The calculated $d_{hkl}$ and intensities are based on $a = 5.995 \pm 0.049$ Å, $b = 3.182 \pm 0.054$ Å, $c = 5.633 \pm 0.010$ Å, and $\beta = 112.13° \pm 0.51°$ with $4i$ positions given by (0.280, 0, 0.252) for the $C2/m$ phase.

| $hkl$ | $d_{\text{calc}}$ (Å) | $d_{\text{obs}}$ (Å) | $I_{\text{calc}}$ | $I_{\text{obs}}$ |
|---|---|---|---|---|
| 200 | 2.776 | $2.770 \pm 0.001$ | 44 | $38 \pm 7$ |
| 11-1 | 2.654 | $2.648 \pm 0.001$ | 100 | $100 \pm 4$ |
| 002 | 2.609 | $2.608 \pm 0.001$ | 51 | $59 \pm 4$ |
| 20-2 | 2.407 | $2.407 \pm 0.001$ | 43 | $16 \pm 1$ |
| 111 | 2.271 | $2.271 \pm 0.001$ | 87 | $48 \pm 1$ |
| 11-2 | 2.103 | $2.103 \pm 0.001$ | 2 | $5 \pm 1$ |
| 31-1 | 1.692 | $1.700 \pm 0.001$ | 28 | $8 \pm 1$ |
| 202 | 1.621 | $1.624 \pm 0.006$ | 14 | $11 \pm 5$ |
| 11-3 | 1.614 | $1.614 \pm 0.002$ | 31 | $4 \pm 2$ |
| 310 | 1.600 | $1.602 \pm 0.002$ | 9 | $26 \pm 5$ |
| 40-2 | 1.478 | $1.472 \pm 0.039$ | 6 | $4 \pm 2$ |
| 20-4 | 1.401 | $1.397 \pm 0.004$ | 7 | $11 \pm 6$ |
| 40-3 | 1.364 | $1.371 \pm 0.002$ | 3 | $27 \pm 9$ |
| 22-3 | 1.198 | $1.198 \pm 0.001$ | 1 | 1 |
| 115 | 0.921 | $0.921 \pm 0.001$ | 1 | $3 \pm 1$ |

Praseodymium crystallizes in the double hcp (dhcp) structure at ambient conditions with measured lattice parameters of $a = 3.672$ Å and $c = 11.833$ Å. The measured lattice parameter for copper pressure marker was $a = 3.614$ Å for the fcc phase at ambient pressure. The pressure was increased gradually in the diamond anvil cell and the dhcp→fcc transformation was observed at 4 GPa, and the fcc→distorted fcc transformation was observed at 7 GPa. The x-ray diffraction recorded for the distorted fcc phase between 7 and 10 GPa were satisfactorily assigned to a hexagonal phase ($hR24$) described by Hamaya *et al.*[10] Figure 1 upper panel shows a fit to a hexagonal $hR24$ phase at a pressure of 9 GPa. However, when the pressure was increased to the 10–12 GPa pressure range, it became clear that the hexagonal $hR24$ fit was no longer satisfactory. The (113) and (202) as well as the (106) and (024) peaks moved apart substantially as seen in the lower panel of Fig. 1 at 15 GPa. Also, when trying to fit the 15 GPa spectrum to $hR24$ phase, none of the high-energy peaks indexed corresponded to the high-energy peaks of the 9 GPa spectrum. The first thought was that upon increasing the pressure above 9 GPa the $hR24$ structure was becoming increasingly distorted from the fcc phase.[10] The hexagonal $hR24$ structure (24 atoms/cell) can be described with three positional parameters, $6c$, $(0,0,z_1)$ and $18h$ $(x, -x, z_2)$. By varying the parameters $x$, $z_1$, and $z_2$ the amount of distortion can be varied from the fcc phase. However, this only effects the intensities and not the interplanar spacing, $d_{hkl}$ and we were not able to get a good fit to the diffraction peak positions with a hexagonal cell at 15 GPa. Recent studies on rare-earth metals cerium,[11] neodymium,[12] and samarium[13] indicate that one of the post-$hR24$ phases is a monoclinic $C2/m$ phase ($Cmcm$, 4 atoms/cell). Indexing the high-quality 15 GPa spectrum (Fig. 1) to $C2/m$ gives a good fit with $a = 5.995 \pm 0.049$ Å, $b = 3.182 \pm 0.054$ Å, $c = 5.633 \pm 0.010$ Å, and $\beta = 112.13° \pm 0.51°$. The observed and calculated interplanar spacing and intensities for the 15-GPa spectrum of $C2/m$ phase are shown in Table I. It is clear from this comparison in Table I, that we have an excellent fit

TABLE II. The comparison of the observed and calculated interplanar spacings $d_{hkl}$ and the observed and calculated intensities for the x-ray diffraction data for praseodymium at 103 GPa. The calculated $d_{hkl}$ and intensities are based on $a = 2.500 \pm 0.004$ Å, $b = 4.967 \pm 0.012$ Å, and $c = 4.531 \pm 0.001$ Å and positional parameter $y = 0.1$ for the $\alpha$-uranium phase.

| $hkl$ | $d_{\text{calc}}$ (Å) | $d_{\text{obs}}$ (Å) | $I_{\text{calc}}$ | $I_{\text{obs}}$ |
|---|---|---|---|---|
| 020 | 2.483 | $2.478 \pm 0.003$ | 6 | 2 |
| 002 | 2.266 | $2.261 \pm 0.005$ | 59 | $21 \pm 4$ |
| 110 | 2.233 | $2.234 \pm 0.001$ | 75 | $39 \pm 4$ |
| 021 | 2.178 | $2.178 \pm 0.001$ | 100 | $100 \pm 1$ |
| 111 | 2.003 | $2.003 \pm 0.001$ | 64 | $45 \pm 1$ |
| 112 | 1.590 | $1.591 \pm 0.001$ | 52 | $15 \pm 1$ |
| 130 | 1.380 | $1.379 \pm 0.001$ | 2 | 1 |
| 023 | 1.290 | $1.292 \pm 0.002$ | 11 | 1 |
| 113 | 1.251 | $1.252 \pm 0.002$ | 7 | $4 \pm 2$ |
| 040 | 1.242 | $1.239 \pm 0.005$ | 3 | $2 \pm 1$ |
| 042 | 1.089 | $1.088 \pm 0.001$ | 44 | $11 \pm 1$ |
| 133 | 1.019 | $1.017 \pm 0.001$ | 3 | $3 \pm 1$ |
| 223 | 0.898 | $0.897 \pm 0.001$ | 1 | 1 |
| 152 | 0.855 | $0.853 \pm 0.001$ | 1 | $5 \pm 3$ |
| 310 | 0.822 | $0.822 \pm 0.001$ | 1 | $3 \pm 2$ |

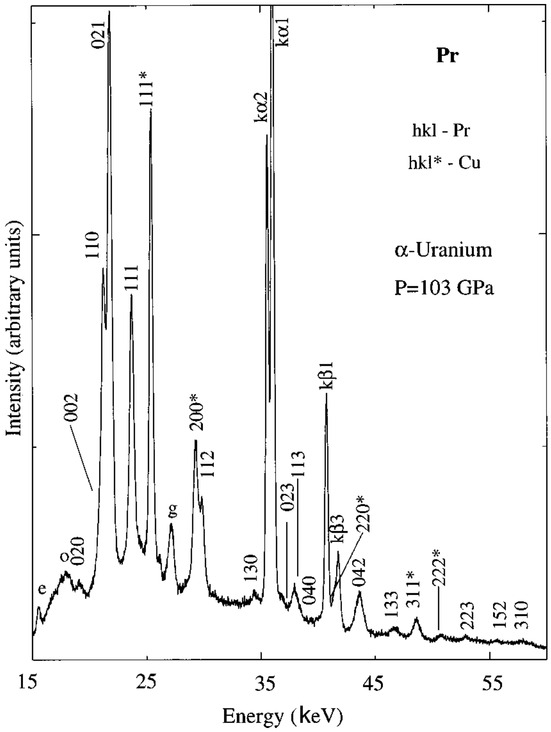

FIG. 2. Energy dispersive x-ray diffraction pattern of Pr sample at the highest pressure of 103 GPa in this study. $Ed = 47.461 \pm 0.008$ keV Å. Pr sample peaks are indexed to an orthorhombic $\alpha$-U phase while copper pressure marker peaks correspond to an fcc phase and labeled by an asterisk. The weak peaks labeled *e*, *o*, and *g* correspond to an escape peak, oxide peak, and gasket peak, respectively.

to the interplanar spacings with this $C2/m$ phase and fit to the observed intensities is satisfactory considering the well-known preferred orientation and grain growth effects in rare-earth metals.[14] It should be added that a previous study[10] fitted $hR24$ phase to the entire pressure range between 7 and 20 GPa in Pr. However, we find that between 10 and 20 GPa pressure range, Pr diffraction patterns can be satisfactorily indexed with a smaller monoclinic $C2/m$ cell with 4 atoms/cell. Therefore, there is no clear need or advantage to define a large unit cell $hR24$ with 24 atoms/cell in this pressure range of 10–20 GPa in Pr where a smaller monoclinic cell can describe the data very well.

At 20 GPa we observed a transformation from monoclinic $C2/m \rightarrow$ orthorhombic $\alpha$-U (4atoms/cell) phase, which is stable up to 103 GPa. Figure 2 shows the energy dispersive x-ray diffraction for Pr at the highest pressure of 103 GPa indexed to the $\alpha$-U phase with $a = 2.500 \pm 0.004$ Å, $b = 4.967 \pm 0.012$ Å, and $c = 4.531 \pm 0.001$ Å. The $\alpha$-U structure in Pr has been confirmed by several previous studies above 20 GPa.[5–7,10] This $\alpha$-U phase is stable to the highest pressure as is clear from the good agreement in the calculated and observed interplanar spacings and intensities at a pressure of 103 GPa (Table II). $\alpha$-U is an orthorhombic distortion of the hcp structure with cell parameters *a, b*, and *c*. The four atoms occupy $4c$ positions with coordinates $(0, y, \frac{1}{4})$, $(0, -y, \frac{3}{4})$, $(\frac{1}{2}, y + \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2} - y, \frac{3}{4})$. The $y$ parameter in the $\alpha$-U phase in most materials is close to 0.1.[15] After varying the $y$ parameter about the 0.1 value we found that $y = 0.1$ did give the best fit to the relative diffraction intensities in Table II.

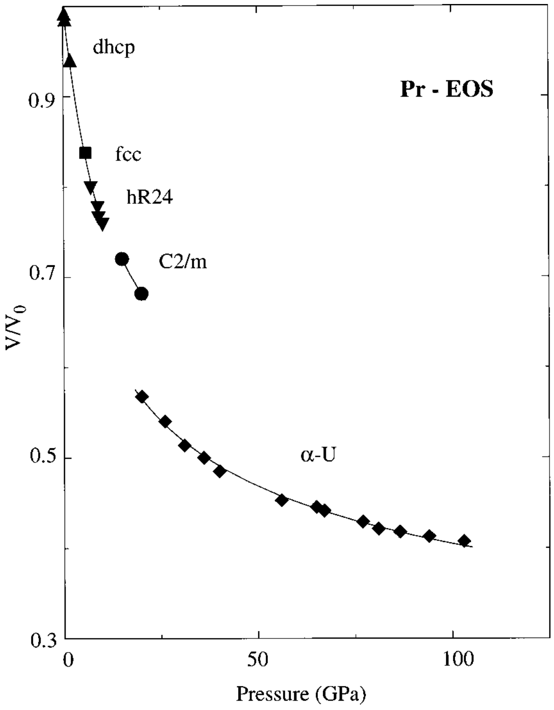

FIG. 3. The measured pressure–volume curve or equation of state for Pr metal to 103 GPa at room temperature. Five different crystallographic phases are labeled in this pressure range. The data below 20 GPa for precollapse phases and after 20 GPa for post-collapse phases are fitted by three different solid curves described in the text.

A significant feature of the monoclinic $C2/m$ phase$\rightarrow$orthorhombic $\alpha$-U phase in Pr is the large volume collapse at the transition. The volume collapse is defined as $\Delta V/V = (V_m - V_\alpha)/V_m = 0.167$ or 16.7% at the transition pressure of 20 GPa, where $V_m$ and $V_\alpha$ are the volumes for the monoclinic and the $\alpha$-U phases, respectively, and can be computed from the equation of state parameters described below.

Figure 3 gives the equation of state of Pr to 103 GPa at room temperature. The dhcp through $hR24$ structure, and $C2/m$ structure are fitted separately from the $\alpha$-U structure due to the volume collapse.

The equation of state employed in this analysis was the modified universal equation of state (MUEOS)[16,17] as described below:

$$\ln H = \ln B_0 + \eta(1-x) + \beta(1-x)^2,$$

where $x^3 = V/V_0$ is the volume compression, $\eta = 1.5(B_0' - 1)$, and $H = Px^2/[3(1-x)]$. $V_0$, $B_0$, and $B_0'$ are the atomic volume, isothermal bulk modulus, and the first pressure derivative of the bulk modulus at ambient pressure. The shock data for copper[18] when fitted to the MUEOS gives $B_0 = 143.7$ GPa, $B_0' = 3.904$, and $\beta = 13.77$. These parameters were employed in our pressure calculations based on copper standard.

The following MUEOS fits for Pr were obtained using the fit parameters as shown below. These three fits, for the low-pressure phases below 12 GPa, and the $C2/m$ phase, and another for the high-pressure $\alpha$-U phase, are shown by the solid curves in Fig. 3: (low-pressure phases) $B_0 = 27.16$

$\pm 0.02$ GPa, $B_0' = 0.096 \pm 0.004$, $\beta = 39.88 \pm 0.02$, $V_0(\mathrm{dhcp}) = 34.538$ Å$^3$/atom for $0 < P < 12$ GPa; ($C2/m$ phase) $B_0 = 27.16 \pm 0.04$ GPa, $B_0' = 1.424 \pm 0.005$, $\beta = 25.25 \pm 0.06$, $V_0(C2/m) = 34.538$ Å$^3$/atom for $12 < P < 20$ GPa; ($\alpha$-U phase) $B_0 = 24.73 \pm 0.01$ GPa, $B_0' = 1.933 \pm 0.003$, $\beta = 22.35 \pm 0.01$, $V_0(\alpha\text{-U phase}) = 29.012$ Å$^3$/atom for $20 < P < 103$ GPa.

We now compare our high-pressure results on Pr with the known behavior of its neighboring elements Ce and Nd and consider some general implications for the entire rare-earth metal series. The neighboring element to the right, Nd, has been recently studied to 155 GPa and has shown a similar transition from the monoclinic ($C2/m$) phase to the $\alpha$-U phase at a considerably higher pressure of 113 GPa.[15] This transition pressure should be compared with the value of 20 GPa for Pr for transformation to the $\alpha$-U phase. In the neighboring element to the left, Ce, the transformation pressure is as low as 5 GPa and the total Gibbs free energy for the monoclinic ($C2/m$) phase and the $\alpha$-U phase is very close and they coexist in the pressure range of 5–13 GPa. Therefore, it is clear that the onset pressure for the $\alpha$-U phase formation increases very rapidly as the $4f$ shell is gradually filled in rare-earth metals. Another interesting aspect of our study is that the monoclinic ($C2/m$) phase, which belongs to a set of crystal structures derived by distorting fcc structure, appears to be a precursor to the formation of the $\alpha$-U phase in rare-earth metals. It would be very instructive to theoretically examine[19] the Gibbs free energy of the monoclinic ($C2/m$) and $\alpha$-U phases in light rare-earth metals at high pressures to elucidate this structural trend and shed light on the details of $4f$-delocalization phenomenon.

We offer the following conclusions based on our x-ray diffraction studies on Pr to 103 GPa at room temperature in a diamond anvil cell.

(1) There is a larger volume collapse than previous measurements have suggested at the $f$ delocalization in Pr at 20 GPa. We measure a volume collapse of 16.7% at 20 GPa from a monoclinic phase ($C2/m$, 4 atoms per cell) to the orthorhombic $\alpha$-uranium phase (*Cmcm*, 4 atoms/cell).

(2) The $\alpha$-uranium phase is stable to the highest pressure in this study to 103 GPa. The measured volume compression for Pr is $V/V_0 = 0.407$ at 103 GPa. We provide the equation of state parameters for both the pre-collapse and post-collapsed phases in praseodymium.

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