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α-uranium phase in compressed neodymium metal

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The light rare-earth metal, neodymium, has been studied up to 155 GPa in a diamond-anvil cell using energy dispersive x-ray diffraction with a synchrotron source. The pressures were calibrated using copper as an internal x-ray pressure standard. A phase transformation from a monoclinic phase ($C2/m$, 4 atoms/cell) to an orthorhombic α-U phase *(Cmcm*, 4 atoms/cell) was observed at 113±6 GPa without any observable volume collapse. The observation of α-U phase in Nd and, previously, in cerium and praseodymium clearly establishes this phase in light rare-earth metals. Our equation of state measurements suggest that delocalization of the *f* shell in Nd occurs without any volume collapse unlike Ce and Pr.

In the periodic table, lanthanide elements, cerium through lutetium, are characterized by unfilled *4f* shells. Actinide elements, thorium to lawrencium, are characterized by unfilled *5f* shells. However, there is a major difference in the bonding behavior in the solid state between these two series of elements, *5f* elements (light actinides) have delocalized *f* electrons, which contribute to bonding in the solid state. On the other hand, *4f* electrons are localized in the lanthanide elements and do not participate in bonding or in influencing the stability of a particular crystal structure. Pressure plays a pivotal role in lanthanide and actinide elements at room temperature. First, it can delocalize the *f* shell, and second it can cause electron transfer between various subbands in the conduction electrons such as $sp \rightarrow d$ and $spd \rightarrow f$ electrons under high pressure. Pressure has a very dramatic effect on the volume in lanthanide and actinide metals, as is demonstrated by a recent study on ytterbium[1] where a compression by a factor of 4 ($V/V_0 = 0.25$) was observed at 2 million atmospheres (200 GPa). Pressure is also known to cause delocalization or Mott transition of the *4f* shell in light lanthanide metals.[2] It should be added that *f*-shell delocalization occurs in a discontinuous manner in cerium and praseodymium. In Ce, a volume collapse of 16% is observed at a pressure of 0.7 GPa,[3] and in Pr a volume collapse of 9% (Ref. 4) is observed at 22 GPa (for a recent summary of volume collapse transitions in rare-earth metals see McMahan *et al.*[5]).

α-uranium phase is associated with the delocalized *f* shell as evidenced by the element uranium amongst the light actinides. Ce, with an electronic configuration $4f^1(spd)^3$, shows a transition to the α-U phase at pressures above 5 GPa. However, the total free energy of the α-uranium structure and the monoclinic $C2/m$ structure in Ce are close. The equilibrium phase, between 5 and 13 GPa, $C2/m$ or α-U, is not established in Ce at the present time.[6] The microstructure of the starting sample can cause a preference of one phase or the other in cerium in the pressure range of 5–13 GPa. The next rare-earth metal in the periodic table, praseodymium, with an electronic configuration $4f^2(spd)^3$, exhibits the α-U structure at 22 GPa with a volume collapse of 9%.[4,7–9] It has not been possible to observe α-U phase in rare-earth metals with higher *f*-shell occupancies greater than 2 because of the multimegabar pressure required. However, recent advances in diamond cell technology coupled with synchrotron-radiation sources have added a new impetus to this field.

Neodymium, a member of the lanthanide series, or more specifically the light rare-earth metals, has an electronic configuration of $4f^3(spd)^3$ and crystallizes in the double hcp (dhcp) structure at ambient conditions. Previous work in the low-pressure range to 40 GPa on Nd has documented the well-known rare-earth crystal structure sequence.[10] This sequence, dhcp→fcc→distorted fcc, is a common structural sequence among rare-earth metals. In addition, a recent study[11] on Nd to 153 GPa reported a transformation from a distorted fcc to a monoclinic $C2/m$ phase at 75 GPa. The $C2/m$ phase in Nd was reported to be stable between 75 GPa and 153 GPa. Our present study is motivated by the expectation of the appearance of *f*-bonded crystal structure like α-U at megabar pressures in Nd.

Nd was studied in a diamond-anvil cell device at room temperature employing copper as in internal pressure standard. Two different experiments were carried out using energy dispersive x-ray diffraction with a synchrotron source to confirm the repeatability of all the observed phase transformations. We employed diamond coated rhenium gasket in both experiments to increase the sample thickness at high pressures and to improve the quality of x-ray-diffraction patterns. In the first experiment, we employed diamonds with a central flat of 65 μm and 7.5° bevel angle to a culet size of 300 μm in diameter, and a sample hole of 50 μm in diameter was filled with a polycrystalline sample of neodymium and copper. In the second experiment, diamonds with a central flat of 35 μm and a 7.5° bevel angle to a culet size of 350 μm in diameter were employed and a sample hole of 25 μm in diameter was filled with Nd and copper marker. For both experiments no pressure medium was considered necessary since neodymium is an extremely soft material and sample oxidation is also a concern with wet pressure media. Energy dispersive x-ray-diffraction spectrums were recorded at the superconducting wiggler beam-line X-17C station at NSLS, Brookhaven National Laboratory. The experiments were performed with a microcollimated x-ray beam of 8 μm×10 μm.

Neodymium crystallizes in the dhcp structure at ambient conditions and the measured lattice parameters are $a = 3.657$ Å and $c = 11.799$ Å. The measured lattice parameter for copper pressure standard was $a = 3.614$ Å for the fcc

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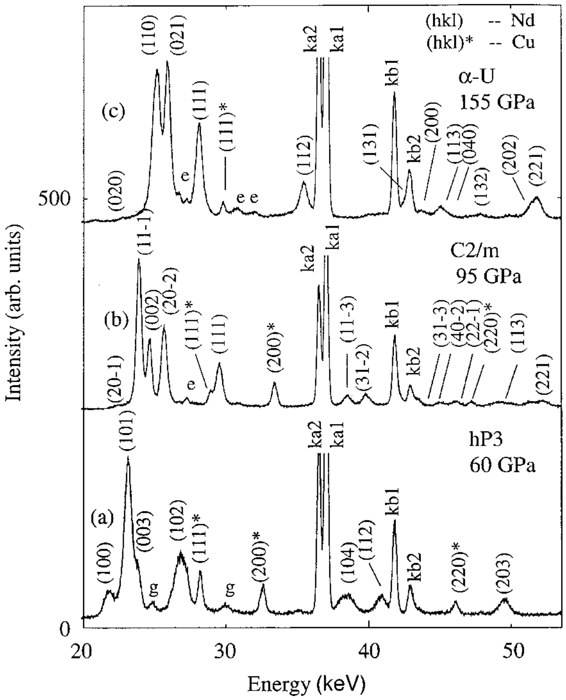

FIG. 1. Energy dispersive x-ray-diffraction spectrum of neodymium sample mixed with copper pressure standard at various pressures. (a) At 60 GPa in the *hP3* phase, (b) at 95 GPa in the *C2/m* phase, and (c) at the highest pressure of 155 GPa in the α-uranium phase. The product of energy and interplanar spacing $Ed=54.795$ keV Å. The peaks labeled *e* are escape peaks from the germanium detector, and $k\alpha$ and $k\beta$ lines are fluorescence emission from the neodymium sample.

phase at ambient pressure. The pressure was increased gradually in the diamond-anvil cell and the dhcp→fcc transformation was observed at 9 GPa, and the fcc→dfcc transformation was observed at 17 GPa. The transformation from dfcc→*hP3* was observed around 35 GPa and from $hP3$ →monoclinic $C2/m$ phase was observed at 75 GPa. These data are in good agreement with previous work.[11–13]

In our experiment another phase transformation occurred at 113±6 GPa from the monoclinic $C2/m$ phase with 4 atoms/cell to the orthorhombic α-U *(Cmcm)* structure with 4 atoms/cell. Figure 1 shows the energy dispersive x-ray-diffraction spectrum of Nd at 60 GPa in the *hP3* phase, 95 GPa in the $C2/m$ phase and 155 GPa in the α-U phase. The transformation from $C2/m$ phase to α-U phase is fairly dramatic with the appearance of a diffraction peak corresponding to (111) and (112) reflections of the orthorhombic phase and disappearance of (111) and (202) reflections of the monoclinic phase. It should be mentioned that this transformation to the orthorhombic phase was missed in an earlier study.[11] Our reexamination of the x-ray data obtained in this earlier study to 153 GPa (Ref. 11) does indicate the presence of the key (111) and (112) reflections of the α-U phase. The observed and calculated interplanar spacing and intensities are in overall good agreement for the α-U structure as shown in Table I. It should be added that the intensity fits for (112), (131), and (200) are poor and we attribute that to overlap with the fluorescence lines, preferred orientation, and large grain-size effects in the energy dispersive diffraction spectrum. The diffraction peak (112) overlaps with *ka* fluorescence lines and (131) and (200) overlap with the *kb* fluorescence lines. In regions where there is no overlap such as (110), (021), and (111), the agreement between the observed and calculated intensities is very good. Image plate x-ray-diffraction experiments on cerium metal at high pressures have shown large grains (or spotty diffraction rings) at the formation of α-U phase at 5 GPa.[14] Similar image plate x-ray-diffraction studies at pressures above 113 GPa on neodymium may provide further insight in to preferred orientation and large grain size effects in the α-uranium phase.

TABLE I. The comparison of the observed and calculated interplanar spacings d_{hkl} and the observed and calculted intensities for the x-ray-diffraction data for neodymium at 155 GPa. The calculated d_{hkl} are based on $a=2.421$ Å, $b=4.788$ Å, and $c=4.340$ Å for the α-uranium phase. The calculated intensities for the α-U phase are based on $y=0.097\pm0.005$.

hkl	$d_{\rm obs}$ (Å)	$d_{\rm calc}$ (Å)	$I_{\rm obs}$	$I_{\rm calc}$
020	2.389	2.394	1	5
110/002	2.162	2.160	100	100
021	2.097	2.096	67	72
111	1.932	1.934	42	46
112	1.532	1.531	16	52
131	1.271	1.274	12	36
200	1.213	1.210	1	8
113	1.204	1.202	5	10
040	1.192	1.197	1	4
132	1.134	1.135	1	1
004	1.088	1.085	1	4
202	1.058	1.057	4	8
221	1.047	1.048	15	14

α-U is an orthorhombic distortion of an hcp structure with cell parameters *a*, *b*, and *c*. The four atoms occupy *4c* positions with coordinates $(0,y,\frac{1}{4})$, $(0,-y,\frac{3}{4})$, $(\frac{1}{2},y+\frac{1}{2},\frac{1}{4})$, and $(\frac{1}{2},\frac{1}{2}-y,\frac{3}{4})$. The *y* parameter in α-U phase in most materials is close to 0.1.[15] We determined the *y* parameter by computing the observed intensities and minimizing the sum of the squares of the difference between the observed and calculated intensities with *y* varying in a step size of 0.005. Our value of $y=0.097\pm0.005$ is in good agreement with data on other materials.

In Fig. 2, we show the axial ratios *b/a* and *c/a* for the three phases of neodymium in the pressure range between 50 and 150 GPa. The $hP3$ and monoclinic $C2/m$ phases can be treated as a distortion of an fcc structure. The unit-cell dimensions of the *hP3* and *C2/m* phases are related to the lattice parameters a_c of the fcc phase.

For hexagonal $hP3$ phase, $a\cong a_c/\sqrt{2}$ and $c\cong\sqrt{3}a_c$, with $(c/a)_{\rm ideal}\cong\sqrt{6}$. We show this ideal value as a solid line for the *hP3* phase in Fig. 2.

For monoclinic $C2/m$ phase, $a\cong\sqrt{6}a_c/2$, $b\cong a_c/\sqrt{2}$, $c\cong\sqrt{6}a_c/2$, and $\beta\cong109.5°$, $(c/a)_{\rm ideal}\cong1.0$ and $(b/a)_{\rm ideal}\cong0.577$ are the values shown by the solid lines shown for the $C2/m$ phase in Fig. 2.

For orthorhombic α-U phase, the unit cell is related to an hcp phase, $a=a_{\rm hcp}$, $b\cong\sqrt{3}a_{\rm hcp}$, and $c=c_{\rm hcp}$, $(c/a)_{\rm ideal}\cong1.633$ and $(b/a)_{\rm ideal}\cong\sqrt{3}$ are the values shown by the

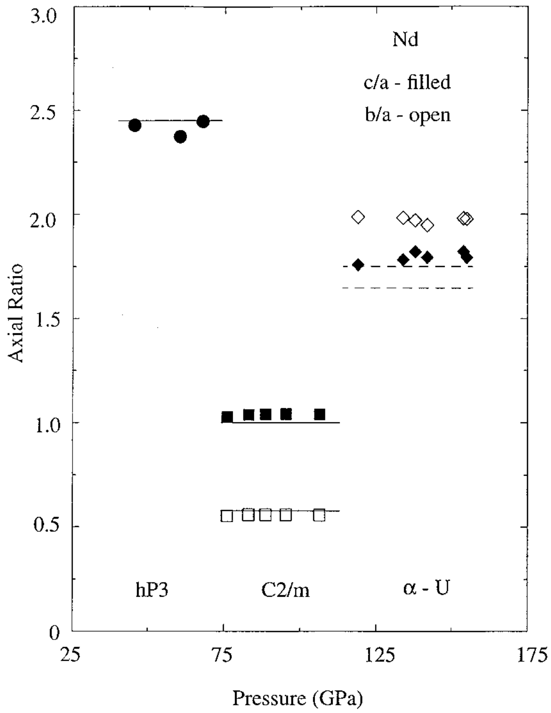

FIG. 2. The axial ratios c/a and b/a for the three crystalline phases in Nd in the pressure range 40–155 GPa. Hexagonal *hP3* phase with *c/a* shown, monoclinic $C2/m$, and orthorhombic α-U phases are shown with both *c/a* and *b/a*. The solid lines are the ideal values based on an undistorted face-centered-cubic structure and the dashed lines are the ideal values based on the hcp structure.

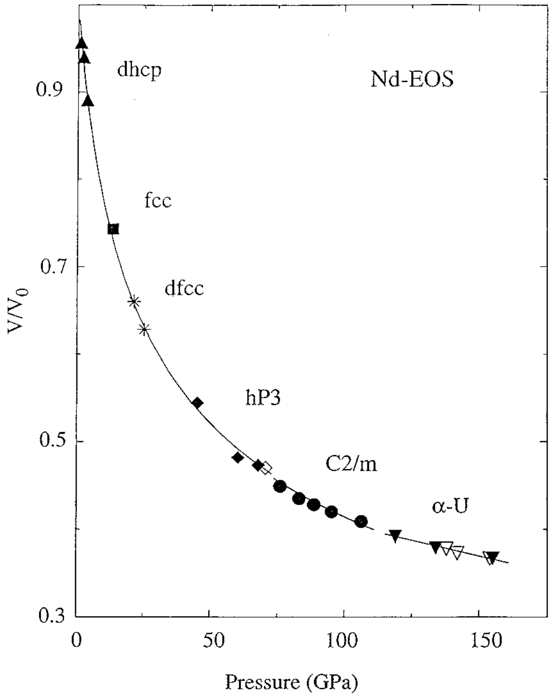

FIG. 3. The measured equation of state of neodymium to 155 GPa at room temperature. The filled symbols represent data obtained from the first experiment while the open symbols represent data obtained from the second experiment. The solid curves are the fits to the modified universal equation of state described in the text.

dashed lines in Fig. 2. It can be seen from Fig. 2 that the experimental values are higher than these ideal values and α-U is considerably distorted from an hcp lattice.

Figure 3 shows the measured equation of state of neodymium to 155 GPa at room temperature. The volume changes associated with these structures do not show any discontinuities or collapse at the transition pressures.

The equation of state employed in this analysis was the modified universal equation of state (MUEOS) (Refs. 16 and 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 give $B_0 = 143.7$ GPa, $B_0' = 3.904$, and $\beta = 13.77$. We employed these parameters in our pressure calculations based on copper standard.

The following MUEOS fits for Nd were obtained using ambient pressure volumes of $V_0(\text{dhcp}) = 34.165$ Å^3/atom: (i) (Low-pressure phases) $B_0 = 25.38$ GPa, $B_0' = 3.119$, and $\beta = 4.075$ for $0 < P < 80$ GPa, (ii) (monoclinic phase) $B_0 = 24.05$ GPa, $B_0' = 3.225$, and $\beta = 3.975$ for $80 < P < 119$ GPa, and (iii) (α-U phase) $B_0 = 6.141$ GPa, $B_0' = 7.351$, and $\beta = 0$ for $119 < P < 155$ GPa.

It is interesting to point out that the monoclinic $C2/m$ phase and orthorhombic α-U phase are quite distinct in Nd under pressure. Our experiments suggest that as pressure increases, monoclinic *C2/m* phase has the lowest free energy between 75 and 113 GPa. As pressure increases beyond 113 GPa, orthorhombic α-U phase becomes the lowest free-energy phase and is stable to at least 155 GPa. First-principles total-energy calculations at high pressure are needed for Nd to confirm these suggestions from our experiments. This behavior of Nd is to be contrasted with Ce where monoclinic $C2/m$ phase and orthorhombic α-U are too close in energy. The equilibrium phase between 5 and 13 GPa in Ce is yet to be established.[6]

We offer the following conclusions: (i) A phase transformation in Nd from a monoclinic phase ($C2/m$ 4 atoms/cell) to an orthorhombic α-U ($Cmcm$ with 4 atoms/cell) is observed at 113±6 GPa. (ii) The observation of a α-U phase clearly establishes a trend in light rare-earth metals. Ce transition to α-U is at 5 GPa, Pr transition is at 22 GPa, and Nd is at 113 GPa. (iii) The measured equation of state of Nd to 155 GPa (volume compression $V/V_0 = 0.36$) does not reveal any volume discontinuities or collapse. We present equation-of-state parameters for all known phases of Nd to 155 GPa. This implies that f delocalization in Nd proceeds in a continuous manner unlike Ce and Pr.

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