PHYSICAL REVIEW B **71**, 012108 (2005)

Crystal grain growth at the α-uranium phase transformation in praseodymium

Nicholas C. Cunningham, Nenad Velisavljevic, and Yogesh K. Vohra
Department of Physics, University of Alabama at Birmingham, Birmingham, Alabama 35294-1170, USA

(Received 3 October 2004; published 31 January 2005)

Structural phase transformations under pressure are examined in praseodymium metal for the range 0–40 GPa at ambient temperature. Pressure was generated with a diamond-anvil cell, and data were collected using high-resolution synchrotron x-ray diffraction and the image plate technique. The structural sequence double hexagonal close packed (dhcp)→face centered cubic (fcc)→distorted-fcc (d-fcc)→α-uranium (α-U) is observed with increasing pressure. Rietveld refinement of all crystallographic phases provided confirmation of the hR24 structure for the d-fcc phase while the previously reported monoclinic phase between the d-fcc and the α-U phase was not confirmed. We observe dramatic crystal grain growth during the volume collapse concurrent with the symmetry-lowering transition to the α-U structure. No preferred orientation axis is observed, and the formation process for these large grains is expected to be via a nucleation and growth mechanism. An analogous effect in rare earth metal cerium suggests that the grain growth during transformation to the α-U structure is a common occurrence in f-electron metals at high pressures.

DOI: 10.1103/PhysRevB.71.012108 PACS number(s): 62.50.+p, 61.66.Bi, 64.70.Kb

INTRODUCTION

High pressure phases of the light lanthanides have been the subject of intense scrutiny in recent years, as they provide an invaluable window to witnessing and understanding the transition of the f-shell electrons from localized to itinerant character, and the related structural changes to open, low-symmetry crystals. At ambient temperature and pressure, the light lanthanides typically exhibit a close-packed structure, and transform under pressure from one to another via *sp* to d-band electron promotion.[1–4] The f-shell is initially well localized and does not participate in bonding, but the Wigner-Seitz radius decreases under pressure more readily than the ionic radius,[5] and eventually the broadened f-shell hybridizes with the *spd* band. At this point the f-shell delocalizes, the f-electrons become available for bonding, and a dramatic volume collapse is observed. This process is responsible for the observed seemingly paradoxical lowering of symmetry under pressure typically displayed by the rare earths.[6–11] Praseodymium (Pr) metal is initially trivalent[12] and close-packed, but at 19 GPa the lattice assumes the open orthorhombic α-uranium (α-U) structure. The α-U structure of the Pr high pressure phase was shown by Smith and Akella,[10] using the experimental data of Mao, Hazen, Bell, and Wittig,[2] and independently by Grosshans, Vohra, and Holzapfel,[13] using the new x-ray data. At this α-U phase transition, electrical resistance measurements[14] and volume calculations[15,16] indicate that the f-shell is delocalized. Recent measurements to 313 GPa (Ref. 17) show a transition to primitive orthorhombic $P2_12_12_1$ at 147 GPa, but no further volume collapse. Praseodymium is predicted to eventually transition to an hcp phase as the symmetry-lowering effect of pressure-induced promotion to the f-band is overwhelmed by the symmetry-raising effects of band broadening and increasing electrostatic energies.[18]

EXPERIMENT

We conducted *in situ* angular dispersive x-ray diffraction measurements on Pr to 40 GPa. X-ray diffraction spectra were collected on HP-CAT beamline 16ID-B at the Advanced Photon Source at Argonne National Laboratories. Two experiments were conducted using monochromatic beams of 0.3683 Å and 0.4155 Å, respectively. Typical beam spot size was 10–15 μm square. Pr of 99.9% purity, purchased from Alfa Aesar, was scoured of accumulated oxide immediately prior to its placement in the sample chamber of a spring steel gasket. No pressure medium was used in the diamond anvil cell due to the high reactivity of the pure metal, but Pr is expected to remain soft enough for quasihydrostatic conditions to prevail. Pressure was measured from the copper diffraction data obtained from the same spatial region as the Pr sample and using an equation of state of copper fitted to third-order Birch-Murnaghan fit.[17] The use of angular dispersive image plates allowed for the capture of a complete cross section of the Debye-Scherrer cone. The wide dynamic range of the plates is capable of resolving and assigning accurate intensities to the weak rings characteristic of low symmetry structures. This permits accurate structural determinations to be made despite the observed significant, though transient, orientation effects. Analysis was carried out primarily using the programs FIT2D,[19] GSAS,[20] EXPGUI,[21] and POWDERCELL.

RESULTS

At ambient pressure, praseodymium crystallizes in a double hcp structure (dhcp), ($P6_3/mmc$), with measured lattice parameters $a=3.662\pm0.003$ Å and $c=11.813\pm0.009$ Å. This structure may be thought of as two hcp phases alternating such that the hexagonal plane sequence is A-B-A-C-A,[22] and hence the axial ratio c/a is twice the hcp value. Pure praseodymium is highly reactive, and some oxidation occurred during loading. Oxide typically consists of a Pr_6O_{11} superstructure corresponding to an ordered $(Pr_2O_3)\cdot4(PrO_2)$ phase, but the small amount of oxide present was indexed satisfactorily as purely PrO_2 in the fluorite (CaF_2)[23,24] structure throughout.

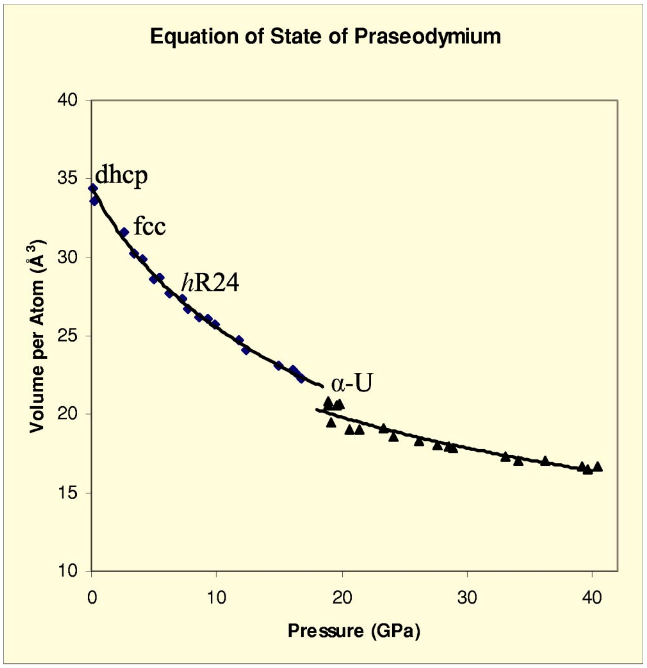

FIG. 1. Equation of state of Pr to 40 GPa. The compressibilities of the first three phases were found to be comparable and are fitted as one single curve. The discontinuity in volume across the transition to α-U is calculated to be 9.1%.

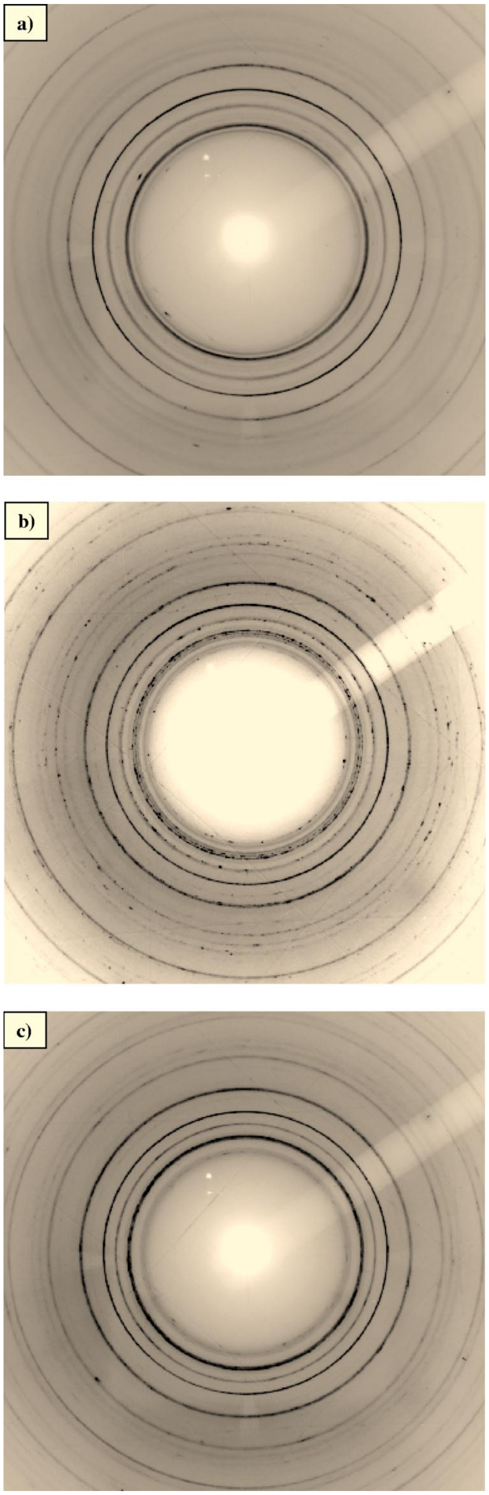

FIG. 2. Evolution of the image plate raw data across the volume collapse. (a) Smooth diffraction rings for the hR24 phase at 16.0 GPa, slightly below the transition to the α-U structure. (b) Dramatic grain growth at 18.9 GPa showing spotty pattern. Note that the bright spots appearing along the Pr rings do not prefer any particular orientation, as would be the case for standard texturing effects. Close examination reveals that the affected rings all belong to the emergent α-U phase. (c) A return to continuous diffraction rings showing near random distribution of grains at a higher pressure of 28.5 GPa.

The smooth transition to another close-packed structure, face centered cubic (fcc), is completed around 4 GPa on compression. At 7 GPa the lattice began to exhibit distortions from the high symmetry close-packed structures, as evidenced by the appearance of several additional weak superlattice peaks. This distorted fcc structure may be indexed according to a hexagonal unit cell (space group 166), *h*R24 structure described by Hamaya *et al.*[25] with atoms occupying two independent atomic positions, 6*c* and 18*h*. This distorted phase coincides with fcc when the three independent fractional parameters have the values $z_1 = 0.25$, $x = 0.5$, and $z_2 = 0.25$. These positions vary gradually as pressure increases, showing less than 5% variation across the entire range.

At 19 GPa, the structure undergoes a sudden collapse in volume of 9.1% (Fig. 1), transforming to the low-symmetry α-uranium structure (*Cmcm*). The refined free lattice parameter y exhibited slightly greater variability than is observed in U itself, varying from 0.099 to 0.104 across the 21 GPa examined in this experiment. This structure was retained through 40 GPa. The compressibility also drops dramatically at this transition. In a third order Birch-Murnaghan fit, the bulk modulus and its first derivative change from 21.70 GPa and 3.03 for the precollapse phases to 27.69 GPa and 3.44 for the α-U structure, respectively. Though the increase in bulk modulus is proportionally significant, it is still expected that the metal is soft enough for quasihydrostaticity to obtain.

The formation of large crystal grains is clearly visible in the angular dispersive image plates (Fig. 2) just as the structure transitions to α-U. Until the transition begins, the diffraction rings remain smooth and continuous, indicating a well-randomized powder. This condition of homogeneity is

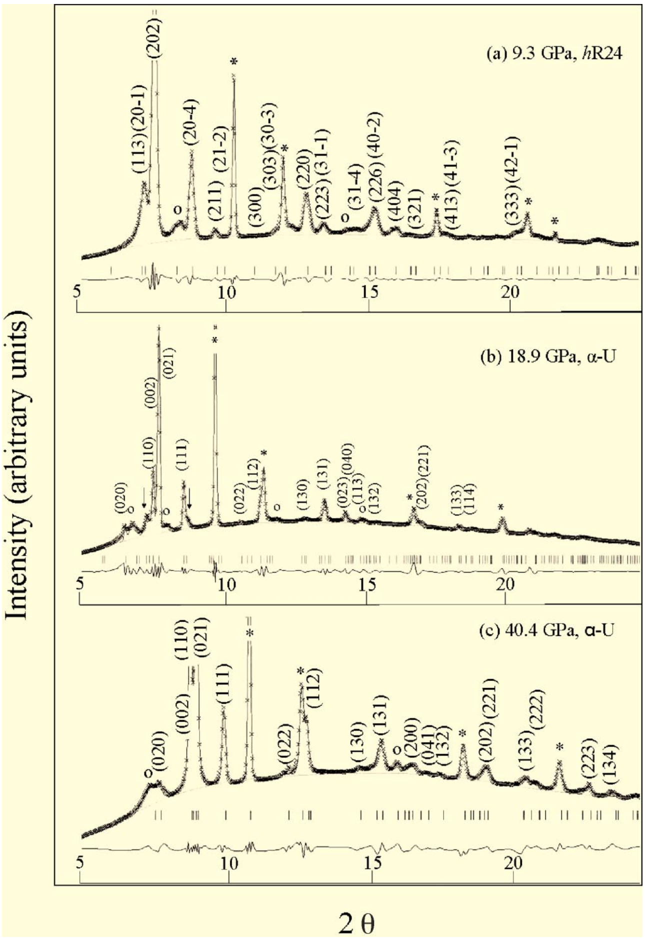

FIG. 3. Refined praseodymium x-ray spectra ($\lambda = 0.3683$ Å) showing the emergence of the low-symmetry α-U phase. Calculated reflection positions are marked by bars. Copper pressure marker peaks are denoted by an asterisk, and oxide peaks with "o." Crosses mark observed data points, and the solid lines represent calculated spectra, background, and the difference between calculated and observed values, respectively. The *hkl* labels are placed according to reflection position, but not intensity. (a) hR24 phase at 9.3 GPa. (b) α-U phase at 18.9 GPa where grain growth is observed, slightly above the transition pressure. Residual hR24 peaks are marked with arrows. (c) Pure α-U phase at 40.4 GPa.

completely restored in the new phase within 4 GPa. A careful examination of the diffraction pattern reveals that only those rings which can be assigned to the lower-symmetry α-U phase exhibit the spottiness characteristic of grain growth. As the refinements in Fig. 3 demonstrate, all expected peaks are present in proper proportion throughout the grain growth regime. This lack of systematic absences and the subsequent return to random orientation of grains indicate that the observed grain growth effect is not related to an alignment of separate crystal grains along the pressure axis. Rather, it is proposed that the phase transition is reconstructive, not displacive, in nature, stemming from the inhomogeneous nucleation and growth of new grains instead of cooperative movement of atoms in the grains.

Bright irregular diffraction spots indicative of the growth of large crystal grains are observed at the volume collapse. These spots occur solely on the postcollapse phase diffraction rings, and grow progressively less frequent and less intense until they entirely fade around 23 GPa. Growth appears to proceed very rapidly upon nucleation, though never to the extent of producing a single crystal as the grains break down readily under pressure. A similar effect is observed in cerium,[26] also at the symmetry-lowering α-U transition; however, that transition occurs after the lone f-electron has become itinerant and the lattice has collapsed isostructurally. It is therefore expected that the grain growth phenomenon is due to the breaking of symmetry, and is only incidentally related to the volume collapse.

In summary, we have studied rare earth metal praseodymium with high resolution image plate x-ray diffraction to high pressures to 40 GPa. Rietveld refinements of the x-ray diffraction phases have been performed and the four crystallographic phases have been confirmed: double hexagonal close packed, face centered cubic, distorted-fcc, and α-uranium. The Rietveld refinement of the distorted-fcc phase confirmed the hR24 structure proposed by Hamaya.[25] An additional monoclinic phase proposed[15] between the distorted-fcc and α-uranium phase could not be confirmed in our detailed structural refinements. In a narrow pressure range of 19–23 GPa, we have observed dramatic crystal grain growth effects in the α-uranium phase as indicated by spotty diffraction patterns. The large grains eventually break up at pressures above 23 GPa and assume a near random distribution giving rise to continuous diffraction rings. This grain growth phenomenon in Pr sample when combined with earlier similar observations in cerium metal[26] indicates that grain growth is fairly common in the α-uranium phase under high pressures. More importantly, this effect is independent of the volume change at the formation of the α-uranium and is attributed to the nucleation and growth mechanisms operative during the formation of α-uranium phase. It is likely that this grain growth phenomenon occurs in all f-electron metals during formation of α-uranium phase under compression. It would be interesting to perform similar studies on $5f$-metal protactinium and $4f$-metal neodymium where αU phase is known to exist under high pressures.

ACKNOWLEDGMENTS

We acknowledge support from the Carnegie/DOE Alliance Center (CDAC) under Grant No. DE-fC03-03NA00144. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Use of the HPCAT facility was supported by DOE-BES, DOE-NNSA (CDAC), NSf, DOD-TACOM, and the W.M. Keck foundation. We thank in particular Dr. H. Liu and M. Somayazulu of HP-CAT for invaluable discussions on structural refinement technique and for their skilled technical assistance.

[1] J. C. Duthie and D. G. Pettifor, Phys. Rev. Lett. **38**, 564 (1977).
[2] H. K. Mao, R. M. Hazen, and P. M. Bell, J. Appl. Phys. **52**, 4572 (1981).
[3] A. Delin, L. Fast, B. Johansson, J. M. Wills, and O. Eriksson, Phys. Rev. Lett. **79**, 4637 (1997).
[4] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).
[5] B. Johansson and A. Rosengren, Phys. Rev. B **11**, 2836 (1975).
[6] A. K. McMahan, C. Huscroft, R. T. Scalettar, and E. L. Pollock, J. Comput.-Aided Mater. Des. **5**, 131 (1998).
[7] F. Porsch and W. B. Holzapfel, Phys. Rev. B **50**, 16 212 (1994).
[8] O. Degtyareva and W. B. Holzapfel, J. Alloys Compd. **322**, 1 (2001).
[9] Y. C. Zhao, F. Porsch, and W. B. Holzapfel, Phys. Rev. B **52**, 134 (1995).
[10] G. S. Smith and J. Akella, J. Appl. Phys. **53**, 9212 (1982).
[11] R. Patterson, C. K. Saw, and J. Akella, J. Appl. Phys. **95**, 5443 (2004).
[12] P. Strange, A. Svane, W. M. Temmerman, Z. Szotek, and H. Winter, Nature (London) **399**, 756 (1999).
[13] W. A. Grosshans, Y. K. Vohra, and W. B. Holzapfel, J. Phys. F: Met. Phys. **13**, L147 (1984).
[14] N. Velisavljevic, K. MacMinn, and Y. K. Vohra, Appl. Phys. Lett. **84**, 927 (2004).
[15] G. N. Chesnut and Y. K. Vohra, Phys. Rev. B **62**, 2965 (2000).
[16] B. J. Baer, H. Cynn, V. Iota, C. S. Yoo, and G. Shen, Phys. Rev. B **67**, 134115 (2003).
[17] N. Velisavljevic and Y. K. Vohra, High Press. Res. **24**, 295 (2004).
[18] P. Söderlind, Phys. Rev. B **65**, 115105 (2002).
[19] A. P. Hammersley, ESRF Internal Report No. ESRF97HA02T, 1997 (unpublished).
[20] A. Larson and B. Von Dreele, computer code GSAS, Los Alamos National Laboratory, 1994.
[21] B. H. Toby, *EXPGUI*, a graphical user interface for *GSAS*, J. Appl. Crystallogr. **34**, 210 (2001).
[22] S. Heathman, R. G. Haire, T. Le Bihan, A. Lindbaum, K. Litfin, Y. Meresse, and H. Libotte, Phys. Rev. Lett. **85**, 2961 (2000).
[23] J. Dabrowski and V. Zavodinsky, in *NIC Symposium 2004 Proceedings*, edited by D. Wold, G. Münster, and M. Kremer (John von Neumann Institute for Computing, Jülich, 2004).
[24] H. J. Osten, J. P. Liu, E. Bugiel, H. J. Müssig, and P. Zaumseil, J. Cryst. Growth **235**, 229 (2002).
[25] N. Hamaya, Y. Sakamoto, H. Fujihisa, Y. Fujii, K. Takemura, T. Kikegawa, and O. Shimomura, in *High Pressure Science and Technology—1993*, edited by S. C. Schmidt *et al.* (American Institute of Physics, New York, 1994), pp. 457–460.
[26] G. Gu and Y. K. Vohra, Phys. Rev. B **52**, 9107 (1995).