Crystal Grain Growth at α-Uranium Phase Transformation in Praseodymium

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Introduction

Chemically, many of the light lanthanides are nigh indistinguishable, but structurally they yield a rich diversity of form. The sequence hcp → Sm-type (9R) → dhcp → fcc observed with increasing pressure or decreasing atomic number across the series is ascribed to variation in *d*-band occupation [1]. The higher angular momentum *f*-electrons are, at ambient pressure, localized well within the interaction radius of the valence *d*-electrons. A variety of low-symmetry structures are observed when decrease of interatomic spacing under pressure forces delocalization into an *f*-band.

Praseodymium, examined here, is a relatively light rare earth and initially exhibits a double hcp structure; the open orthorhombic α-U structure is observed after 19 GPa. Simultaneously, a large collapse in volume per atom is observed as the *f*-electrons leave their separate atomic shells and join the hybrid valence band. Spatial extent and orientation of the "buried" shells in the crystal lattice are not readily observable through other means. Of particular interest here is the observation of large grains at the delocalization pressure, indicating that a reconstructive reseeding process occurs at the transition. A detailed analysis of the processes whereby the group-subgroup symmetry relations are broken in this transition will be forthcoming.

Methods and Materials

We conducted *in situ* angular dispersive x-ray diffraction measurements on powdered praseodymium. X-ray diffraction spectra were collected on HP-CAT beamline 16ID-B at the Advanced Photon Source at Argonne National Laboratories. The brilliance of the beam and the typical beam spot size of 10 – 15 μm square are of enormous value when examining the small samples necessary in high pressure research. Pr of 99.9% purity, purchased from Alfa Aesar, was scoured of accumulated oxide immediately prior to loading. 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 quasi-hydrostatic conditions to prevail. This assumption is confirmed by lack of observed orientation effects. Pressure was measured by fitting the diffraction intensities of an embedded copper marker to 3rd order Birch-Murnaghan fit [2]. 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. Subsequent analysis was carried out primarily using the programs Fit2D [3], GSAS [4], EXPGUI [5], and PowderCell.

Results

A deeper analysis of the data is still being conducted, but Rietveld refinement of all structures indicates that there is only one intermediate phase between the sequence of close-packed structures listed above and full delocalization at 19 GPa. Electrical measurements [6] indicate that the *f*-electrons suddenly enter the valence band at the symmetry-lowering transition, but there is some dispute over the phase immediately preceding. Emergent superlattice reflections indicate that it is some displacive distortion of the fcc structure, but several different structures have been reported[7,8,9]. Fig. 1, taken at 16 Gpa, indicates that the *h*R24 structure proposed by Hamaya *et al.*[10] describes the structure throughout the intermediate region.

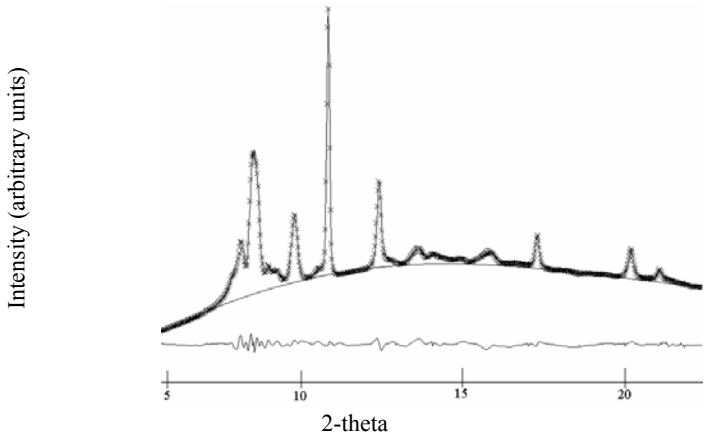

Fig. 1. Refined difference curve showing *h*R24 structure at 16Gpa. Atoms occupy two independent atomic positions, 6c and 18h.

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. This effect has not been reported previous to this work (see [11], forthcoming). An analogous effect is observed in cerium [12] at its symmetry-lowering transition to α-U structure. At this point, Ce has already undergone its volume collapse. The use of image plates capable of capturing complete diffraction rings was critical to determining that the observed orientation effects occur solely in the post-delocalization phase.

Discussion

The observation of grain growth in a second rare earth raises the interesting possibility of using the phenomenon as a window into the underlying transition mechanism. However, the narrowness of the pressure band where grains are visible makes it unlikely that an unpredicted transition will be observed by chance. Furthermore, careful refinement and analysis are required to definitively distinguish grain growth from more standard orientation effects. The generality of the formation of large grains at a symmetry-lowering phase transition remains to be determined. It is intuitively expected to be a feature of any reconstructive transition, a direct

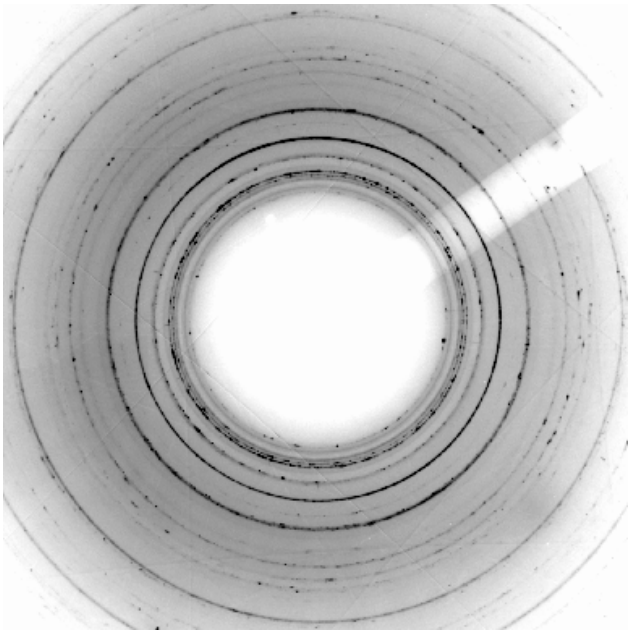

Fig. 2. Dramatic grain growth at 18.9 GPa showing spotty pattern. Note that the intense spots appearing along the Pr rings do not prefer any particular orientation, as would be the case for standard texturing effects. Close examination reveals that the affected rings all belong to the emergent α-U phase.

consequence of the reseeding process. However, the dramatic loss of symmetry or even some peculiarity of the α-U structure itself might play crucial a role in the observation of grains, or their size and the pressure range over which they are observed.

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