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Report:

The aim of this project is to resolve the outstanding question of the distorted *fcc* structure in light rare earths. For the high pressure x-ray diffraction studies in a diamond anvil cell (DAC), it is necessary to have finely grained samples to ensure good powder averaging and to minimize preferred orientation effects. For these reasons, we have developed a technique to prepare samples of lanthanide metals for studies in a DAC. We have also utilized different approaches to extract the structural information from the measured x-ray diagrams using the Rietveld refinement technique. Below, we present details of our work on the preparation, data collection and analysis of the praseodymium sample. Similar approaches have been applied to lanthanum and samarium.

Pr (Alfa, 99.99%) was hydrided at 973 K to form PrH_x. This hydride (1 g) was mixed with 1 g Ta powder (Alfa, 99.9 %, < 2 micron) by grinding in a dry box, spread on a Mo foil with a large area (50 ≈ cm^2), and dehydrided under dynamical vacuum at 823 K for 5 h. The fine powder (appr. 50 %) was lightly brushed from the Mo foil leaving the larger particles adhering to the foil. Optical examination of the resulting Pr-Ta powder mixture revealed that metal particles had sizes less than approximately 2 microns. Such a sample and ruby chips were loaded into the gasket of the DAC under an oxygen-free dry nitrogen atmosphere. No pressure medium was used in order to avoid sample contamination. Angle-dispersive x-ray powder diffractograms measured on the ID9 beamline were collected for several sample loadings to check the reproducibility of the results. Annealing was carried out with an external furnace at 423 K. Structural data were obtained by full Rietveld profile refinements using the program GSAS with two phases (Pr and Ta) refined simultaneuosly. The structural and profile parameters for each phase were: cell constants, the fractional coordinates, isotropic thermal parameters, and Stephens peak function. The global and textural parameters were: Chebyshev polynomial background and March-Dollase correction for preferred orientation in Pr. We found that even after annealing of the Pr/Ta mixture at the high pressure range studied here and at temperatures of about 423 K, there is no alloying of the two metals. In the subsequent data analysis, we used the pressures obtained with the Ta pressure gauge [1], as this metal's *bcc* lattice parameter can be directly extracted from the measured patterns and the two-phase Rietveld refinements.

When the observed diagrams are carefully analysed, one sees that the onset of a phase transition from the *fcc* phase is first observed at about 7.5 GPa with the appearance of the superlattice peaks. At slightly higher pressures, the (111) reflection of the ideal *fcc* lattice ($Fm\bar{3}m$) splits. From the pressure evolution of x-ray diffraction peaks related to the (111) reflection in the *fcc* lattice, it is clear that at pressures above about 13 GPa a triplet is unambiguously resolved, indicating that the symmetry of the distorted *fcc* structure in praseodymium is not higher than the orthorhombic one. On the other hand, a presence of only two (201) and (220) peaks, both related to the *fcc* (111) reflection, is possible in the *Cmmm* and *Cmma* space groups, that were previously considered as the best possible orthorhombic candidates for the distorted *fcc* structure [2]. This clearly points out towards a monoclinic structure derived from ideal *fcc*. After the analysis of pressure dependencies of all the observed peaks in the *d-hcp*, *fcc*, and distorted *fcc* structures of Pr we were able to obtain unique sets of peaks only due to the distorted *fcc* structure at different pressures. All of them can be indexed on the basis of the *C2/m* lattice proposed by Zachariasen for cerium [3]. Zachariasen showed that the distorted *fcc* structure of cerium could be well explained by the *C2/m* unit cell with four atoms at the *4i* site (x,0,z) . In the case of the ideal *fcc* structure, the *C2/m* metric lattice parameters a, b, and c are related to the cubic parameter a_{fcc}: $a = c = \sqrt{\frac{3}{2}}\, a_{\mathrm{fcc}}$ and $b = \frac{\sqrt{2}}{2} a_{\mathrm{fcc}}$. The monoclinic β angle is $\beta = \arccos(\frac{\sqrt{3}}{3}) = 109.47°$. These conditions no longer hold for a distorted lattice. At the onset of the phase transition from the *fcc* to distorted *fcc* lattices, the parameters a, b, and c start to diverge. In addition, there is a continuity in the pressure dependence of the unit cell volume. Figure 1 presents the Rietveld refinement of the pattern at 15 GPa after annealing at 423 K for 3 hrs. The Stephens profile function used here incorporates the anisotropic peak broadening due to a strain so that it is indispensable for the high pressure *in situ* x-ray diffraction experiments with an uniaxial compression component in a diamond anvil cell or large volume device (non- and quasi-hydrostatic conditions). Even without any preferred orientation correction, the refinement converges at a respectable value of $R(F^2) = 11.4\%$. On the other hand, when we use other profile functions for x-ray diffraction, as implemented in GSAS, the preferred orientation needs to be accounted for with a high order spherical harmonics expansion for the refinement to arrive at a comparable $R(F^2)$ factor. It should be emphasized that a lack of severe preferred orientation effects in our samples is attributed to small sizes of the Pr and Ta particles as prepared with our synthesis technique.

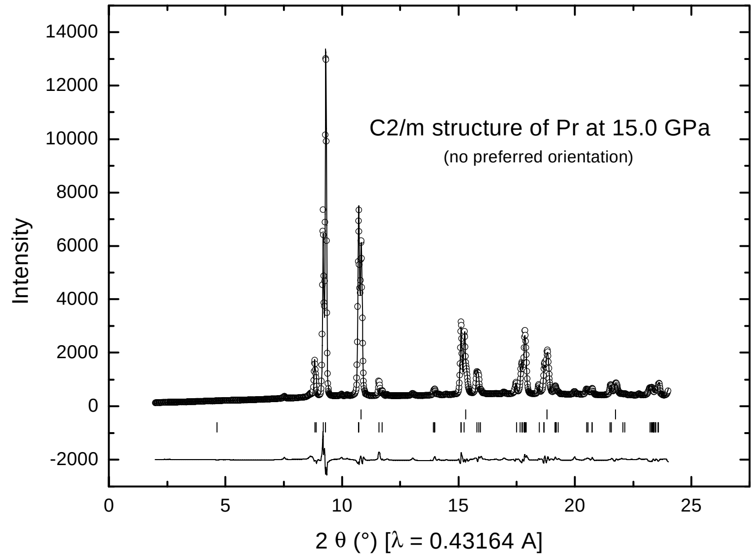

Figure 1 Observed, calculated, and difference x-ray diffraction profiles of the *C2/m* phase of praseodymium at 15.0 GPa. The upper and lower rows of vertical markers indicate Bragg reflections for tantalum and praseodymium, respectively.

References

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3. W.H. Zachariasen, *Proc. Natl. Acad. Sci. U.S.A.* **75**, 1066 (1978); M.I. McMahon and R.J. Nelmes, *Phys. Rev. Lett*. **78**, 3884 (1997).