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LETTER TO THE EDITOR

Crystal structure of the distorted FCC high-pressure phase of praseodymium

N Hamaya†, Y Sakamoto‡, H Fujihisa†, Y Fujii§, K Takemura¶, T Kikegawa|| and O Shimomura||

† Department of Physics, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan

‡ Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

§ Institute for Solid State Physics, University of Tokyo, Minato-ku, Tokyo 106, Japan

¶ National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

|| Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305, Japan

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Abstract. Using synchrotron radiation and an imaging plate we have performed a high-angular-resolution powder x-ray diffraction study of the 'distorted FCC' high-pressure phase of praseodymium. The crystal structure of this phase is identified as the trigonal space group $R\bar{3}m$ (D_{3d}^5) with eight atoms in the rhombohedral unit cell. The observed pressure dependence of atomic positional parameters provides quantitative evidence of an occurrence of the continuous distortion of the FCC lattice. The observed atomic displacement pattern implies that the softening and condensation of a zone-boundary transverse phonon mode at the L point of the Brillouin zone drives this phase transition.

The trivalent lanthanides (Pr to Lu, except for Eu and Yb) exhibit the crystal-structure sequence HCP \rightarrow Sm-type \rightarrow DHCP \rightarrow FCC as a function of increasing pressure [1–3]. An effect of pressure on electronic structure of these metals is to lower the d state relative to the s and p states and to induce the s–d transfer of conduction electrons. It is now well established [4] that the structural sequence of the lanthanides results from the increase of d-band occupancy with pressure through its contribution to the cohesive energy.

Report of anomalies in electrical resistivity in the FCC structure of La [5] and Pr [6] first suggest the possibility of additional phase transitions at higher pressures. Subsequent high-pressure x-ray measurements [7, 8] reveal that the FCC structure transformed into a new structure, which is referred to as 'distorted FCC'. Recently, it has been demonstrated [9] that the distorted FCC phase is the fifth, common member of the lanthanide sequence. Since the FCC-distorted FCC transition appears not only in lanthanides but also in La and Y [8], where there are no occupied f states, this structural change may be understood within the framework of the d-occupancy picture. While the distorted FCC phase is the ultimate high-pressure phase of La and Y, most of the lanthanide metals exhibit loose-packed, low-symmetry structures at higher pressures. This structural change is generally regarded as resulting from the delocalization of 4f electrons.

An attractive feature of the FCC-distorted FCC phase transition lies in its second-order nature [5, 6, 8]. This, together with the s–d transfer, invokes interesting questions concerning the complex interrelations of lattice instability, phonon softening and Fermi surface topology [10, 11]. The knowledge of this transition, however, is very limited. Even its crystal structure is not uniquely determined, though various proposals have been presented [7, 8, 12, 13].

In this letter we report the results of the synchrotron x-ray diffraction study of the distorted FCC phase of Pr. We have performed Rietveld analysis and propose the crystal structure with trigonal space group $R\bar{3}m$ (D_{3d}^5), which is different from space group $P3_221$ (and its enantiomorph) suggested by Vohra *et al* [12]. The displacements of the Pr atoms from their close-packed positions in the FCC lattice develop continuously with pressure above the transition pressure of $P_c = 7$ GPa. The analysis of atomic displacement patterns suggests that the softening of the TA phonon mode at the zone-boundary point L in the Brillouin zone of the FCC lattice drives the FCC-distorted FCC phase transition.

Synchrotron x-ray diffraction measurements were carried out at BL-6B of the Photon Factory at KEK. The incident beam was monochromatized with Si(111) double crystals to a wavelength of 0.6888 Å and collimated to 80 μm in diameter at the sample position. To achieve high angular resolution and reliable intensity collection over a wide dynamic range, an imaging plate was used as a detector. A typical full-width at half-maximum of a reflection was about 0.16° in 2θ . The detail of the present high-pressure x-ray diffractometry has been described elsewhere [14]. Measured diffraction patterns were indexed, corrected for the absorption by the diamonds and the sample, and analysed with the Rietveld program developed by J K Cockcroft of Durham University. A small chip of the sample, which was cut from a polycrystalline rod purchased from Koch-Light Ltd under silicone oil, was compressed in a gasketed diamond anvil cell. Pressure was determined by a ruby fluorescence method [15].

The DHCP phase of Pr transforms to the FCC phase at 6 GPa. The subsequent phase transition to the distorted FCC phase at 7 GPa is accompanied by the appearance of very weak superlattice reflections which are associated with an enlargement of the unit cell. Simultaneously, broadening of the fundamental reflections, except for those having indices $h00$, takes place. A typical diffraction pattern of the distorted FCC phase is shown in figure 1. The intensity of superlattice reflections continuously increases with increasing pressure, as previously reported [8]. Each of the broad reflections splits progressively into two or more peaks as the pressure is raised. The α -uranium-type structure appears about 15 GPa.

Before describing the details of the structure determination, we comment on the contamination of the sample. We observed that in measured diffraction patterns six weak peaks, showing a relative intensity of less than 2%, exist independently of the change in crystal structure of Pr. Very small shifts of all these six peaks with pressure indicate that they arise from a material much less compressible than any structures of Pr. Interplanar spacings of four peaks out of six can be consistently interpreted as those for PrO having the rock-salt type structure with a lattice constant of 5.03 Å at 1 atm [16]. Thus, we have treated the sample as the two-phase system, Pr and PrO, in the Rietveld analysis. The origin of the other two peaks could not be identified.

Determination of the crystal system of the distorted FCC phase is rather straightforward. The 200 and 400 reflections of the FCC structure remain as single peaks in the distorted FCC phase, whereas the other reflections, 111, 220, 311, and 222 split into two or more peaks. This behaviour can be interpreted by the formation of a rhombohedral lattice. In fact, the observed interplanar spacings of the fundamental and superlattice reflections, except for the six peaks described above, are perfectly indexed for a hexagonal cell with $a \simeq \sqrt{2}a_0$ and $c \simeq 2\sqrt{3}a_0$ with $Z = 24$, where a_0 is the lattice constant of the cubic lattice. This new cell can be obtained by doubling both the c axis and a axis of the hexagonal cell for the FCC lattice.

In the course of profile analysis, we were aware that measured diffraction patterns were affected by systematic preferred orientation of sample grains. The difference between the observed and calculated intensities is largest for the $00l$ reflection and decreases

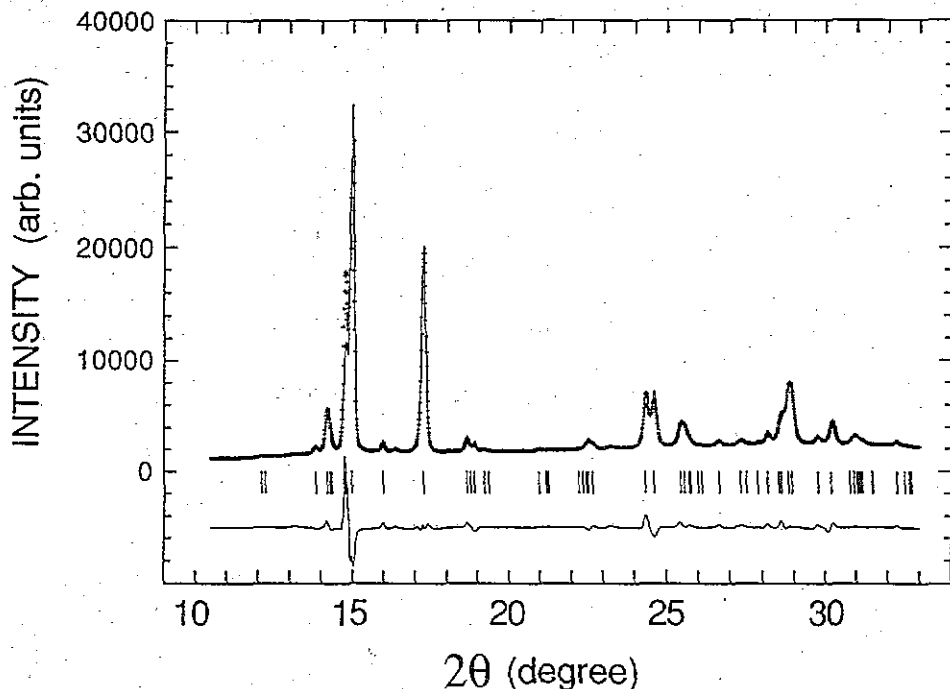


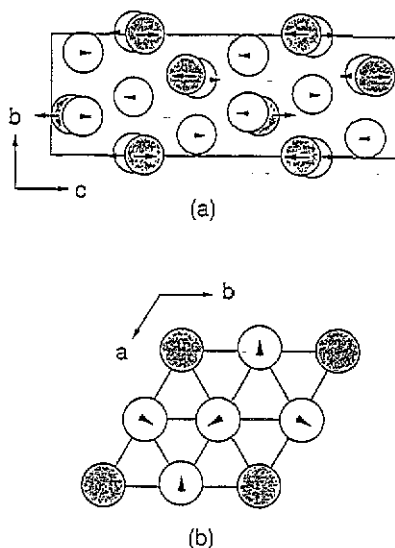
Figure 1. Results of the Rietveld refinement of the distorted FCC phase at 13.8 GPa. The experimental data are given by the crosses and the calculated positions of the reflections by the bars. The difference ($I_{\text{obs}} - I_{\text{calc}}$) curve is also shown. Data points in the region $14.4^\circ - 15.6^\circ$ were not used in the analysis (see text).

exponentially as the indices h and k of the hkl reflection become larger. This effect can be seen at the 006 reflection located at $2\theta = 14.76^\circ$ in figure 1. Since the Rietveld program used in this study is not capable of handling the preferred orientation effect, we have carried out the refinement of the structure using the diffraction data from which the data points of the 006 and adjacent strong 202 reflections are excluded.

We have begun the profile analysis with the choice of a model space group of $R\bar{3}$ (C_3^2), which is the lowest symmetry of all rhombohedral space groups. Resulting values of positional parameters were carefully examined and compared with each other in order to seek a space group with higher symmetry. After several trials, we find that the two space groups $R32$ (D_3^7) and $R\bar{3}m$ (D_{3d}^5) give the same, minimum R_{wp} - factor of 11.8%. In the subsequent refinement process concentrated on these two space groups, particular attention was paid to the reproducibility of the observed intensities of the superlattice reflections, since the distortion of the FCC lattice manifests itself most sensitively in these intensities. Finally the space group $R\bar{3}m$ (D_{3d}^5) is found to reproduce the observed diffraction patterns better. The result of the Rietveld analysis is shown in figure 1. In this structure, the Pr atoms occupy two independent atomic positions with three positional parameters: $6c$: $(0, 0, z_1)$ and $18h$: $(x, -x, z_2)$ in the hexagonal representation. The undistorted FCC structure is obtained when $x = \frac{1}{2}$ and $z_1 = z_2 = \frac{1}{4}$. The structural parameters of the rhombohedral phase at 13.8 GPa are listed in table 1 along with the lattice constant of PrO and the d spacings of two unidentified peaks. It should be noted that Mao's data [7] taken at a similar pressure of 14.4 GPa contain d spacings corresponding to the 111, 200, 220, and 311 reflections of

Table 1. Structural parameters of the distorted FCC phase of Pr at 13.8 GPa in the hexagonal representation.

Space group	$R\bar{3}m (D_{3d}^5)$
Lattice constant (\AA)	$a = 6.4699(1), c = 16.102(3)$
Atomic position	6c: (0, 0, 0.2716(6)) 18h: (0.5104(2), -0.5104(2), 0.2423(5))
PrO ($Fm\bar{3}m$): $a = 4.9593(9) \text{\AA}$	
Unidentified peaks: $d = 2.390 \text{\AA}$ and $d = 1.690 \text{\AA}$	

**Figure 2.** Atomic arrangement of the rhombohedral structure at 13.8 GPa (a) viewed along the a axis and (b) in the (001) plane at $z \simeq \frac{1}{4}$. Hatched and open circles denote the Pr atoms at the 6c and 18h sites, respectively. Arrows indicate the direction of the atomic displacement from the close-packed position.

PrO and one unidentified peak with $d = 1.690 \text{\AA}$.

Figure 2(a) illustrates the atomic arrangement of the rhombohedral structure with parameters given in table 1 viewed along the a axis. The Pr atoms occupying the 6c site move from their close-packed positions in the FCC lattice only in the [001] direction corresponding to the $[111]_{\text{FCC}}$ direction. The atoms at the 18h site display the antiphase movement along the c axis with respect to the 6c atoms in the same layer. In the (001) plane at $z \simeq \frac{1}{4}$, shown in figure 2(b), the 18h atoms move in either the $[110]$, $[1\bar{1}0]$, or $\bar{1}\bar{1}0$ direction in such a way that one type of triangle with three 18h atoms at the corners shrinks and the other type of triangle expands. It is worth pointing out that each of the 18h atoms is displaced approximately parallel to either the $[110]$, $[011]$, or $[101]$ direction of the undistorted FCC structure.

The distortion of the FCC lattice can be expressed by the amplitudes of the static displacements, $\epsilon = x - \frac{1}{2}$, $\delta_1 = z_1 - \frac{1}{4}$, and $\delta_2 = z_2 - \frac{1}{4}$. The continuous character of the FCC-rhombohedral transition is clearly seen in figure 3 where ϵ , δ_1 , and $-\delta_2$ are plotted as functions of pressure. Large error bars on the data points below 8 GPa are due to the weakness of the superlattice reflections. The most important observation in figure 3 is that

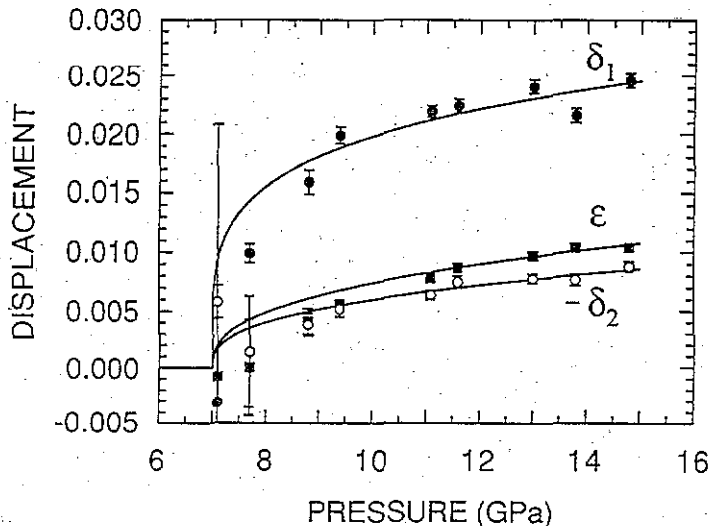


Figure 3. Pressure dependence of static atomic displacements, ϵ , δ_1 , and $-\delta_2$ in the rhombohedral phase. The solid lines correspond to the least-squares fitting of the data to the power law $A(P - P_c)^\beta$, where A and β are fitting parameters and P_c is assumed to be 7 GPa: $\beta = 0.38 \pm 0.06$ for ϵ ; $\beta = 0.22 \pm 0.06$ for δ_1 ; $\beta = 0.37 \pm 0.10$ for δ_2 .

over the whole stability field of the rhombohedral phase, $-\delta_2$ is approximately equal to ϵ and to one-third of δ_1 , namely, $\delta_2 \simeq -\epsilon \simeq \frac{1}{3}\delta_1$. We find that the relationship $\delta_2 = -\epsilon = -\frac{1}{3}\delta_1$ can be derived from the interrelations between the amplitudes of atomic displacements given by a linear combination of three, zone-boundary TA phonon modes, having an equal amplitude, with wavevectors $q_1 = (2\pi/a_0)(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$, $q_2 = (2\pi/a_0)(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $q_3 = (2\pi/a_0)(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ in the FCC structure. This choice of wavevectors is consistent with the fact that the unit cell volume of the rhombohedral phase is eight times larger than that of the undistorted FCC phase. The observed direction of static displacements is also reproduced by the linear combination of those phonon modes. Therefore, we suggest that the FCC-rhombohedral phase transition in Pr is associated with the softening of the TA phonon mode at the L point of the Brillouin zone.

Although no experimental evidence of the phonon softening in the lanthanides with the FCC structure under pressure has so far been reported, it is inferred theoretically by Glocker and Fritsche [17] and Pickett *et al* [11]. Measurements of phonon dispersion curves in FCC-La at 1 atm by Stassis *et al* [18] demonstrate that the TA[111] branch is the lowest-lying one. Together with these implications, the present results strongly suggest that the structural instability of the FCC phase of the lanthanides is induced by the phonon softening, which must originate from the electronic instability.

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