Evidence for 4f-shell delocalization in praseodymium under pressure

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Praseodymium metal undergoes a crystallographic phase transformation from a distorted fcc lattice to a distorted hcp structure at a pressure of $\simeq 210$ kbar. The phase change is accompanied by a large volume decrease of $\simeq 19\%$. This decrease is analogous to the volume collapse at the γ-α transition in cerium and thus provides strong evidence for a delocalization of the $4f^2$ configuration into a $4f$ conduction band.

At a pressure of approximately 200 kbar the rare-earth metal praseodymium (Pr) undergoes transition accompanied by features that are similar to those of the pressure-induced electronic transition in cerium.[1,2] In the low-pressure phases, i.e., γ-Ce and Pr III,[3] the resistance-temperature (R-T) characteristic is anomalous in comparison with simple metals. The temperature coefficient is extremely small between room temperature and 100 K. Below 50 K, however, the resistivity drops precipitously. In contrast, the R-T curve is not anomalous in either high-pressure phase (α-Ce or Pr IV). Because of this similarity between Pr and Ce it has been suggested that the Pr III–Pr IV transition may be analogous to the γ-α transition in Ce.[2] The latter transition has been a perplexing problem in metal physics. It has been assumed that the $4f$ electron in Ce is shifted to the standard deviation (s.d.) conduction band with pressure. Recent reports, however, describe a delocalizaiton of the $4f$ electron itself.[4] The present study was undertaken to investigate the crystal structures and, particularly, the densities of Pr III and Pr IV at high pressure in order to determine whether a volume collapse similar to that at the γ-α transition in Ce may occur at the Pr transition.

The sample was from the same batch of reagent-grade Pr as the one employed in Ref. 2. The polycrystalline sample, ruby powder, and a petroleum jelly pressure-transmitting medium were placed in the sample aperture of a full-hardened T301 stainless-steel gasket and raised to high pressure in a diamond-window, high-pressure cell.[5] The pressure was determined by observation of the calibrated shift of the R_1 flourescent line.[6] Debye-Scherrer x-ray diffraction patterns were obtained *in situ* at high pressure. In these experiments three separate high-pressure cells were employed, and samples were reloaded four times for individual sets of measurements. Twelve experimental points were obtained from which unit cell dimensions at five pressures were determined (Table III).

X-ray diffraction photographs of Pr III contain as many as 20 lines with $\sin \theta / \lambda \leqslant 0.43$. Eight of these reflections, including the three most intense lines, correspond in position and intensity to the (111), (200), (220), (311), (222), and (400) reflections of a fcc structure with cubic axis $a' \cong 4.5$ Å. A well-separated doublet for the (111) reflection, as well as additional weaker lines, however, is evidence for a more complex structure closely related to fcc by lattice distortions. The x-ray powder diffraction patterns were indexed for an orthorhombic phase. Unit cell dimensions were calculated by least-squares procedures from all indexed data with the program LCLSQ.[7] A list of observed and calculated spacings appears in Table I.

The Pr III orthorhombic unit cell is simply related to the fcc subcell: $a \approx b \approx \sqrt{2} a'$ and $c \approx 2a'$. The volume of the orthorhombic cell is four times that of the fcc subcell, and Z is thus assumed to be 16 atoms per unit cell. The relationship between the ideal fcc and orthorhombic Pr III is illustrated in Fig. 1. Actual atomic positions in Pr III are distorted from ideal positions, but the exact fractional coordinates could not be determined from the limited powder diffraction data. The maximum possible space-group symmetry is $P2/m2/m2/m$, and site symmetry of the Pr atom is therefore reduced from $m3m$ in the ideal fcc structure to no greater than mmm in Pr III. For $Z = 16$, the volume per atom ranges from 24.1 to 21.5 Å^3/Pr between 144 and 212 kbar, as illlustrated in Fig. 2. The transition pressure of Pr III was not determined, but it should be noted that the volume per atom versus pressure points of Pr III fall close to an extrapolation of the curve for Pr II (a point determined on the Pr II cruve is listed in Table III).
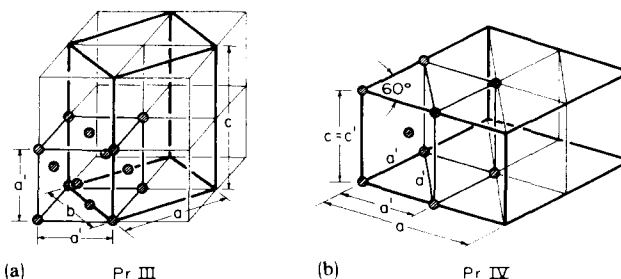

(a)   Pr III   (b)   Pr IV

FIG. 1. (a) Relationship of orthorhombic Pr III to ideal fcc. (b) Relationship of hexagonal Pr IV to ideal hcp.

TABLE I. Calculated and observed powder pattern for Pr III at 144 kbar. [a]

h	k	l	d_{obs}	d_{calc}	$I_{\text{obs}}(\%)$	Equivalent fcc (hkl)
2	1	1	2.768	2.775	50	
2	0	2	2.663	2.664	60 ⎫	111
0	2	2	2.624	2.632	100 ⎭	
2	1	2	2.479	2.468	20	
2	2	0	2.282	2.288	10	200
2	1	3	2.110	2.113	20	
2	3	1	1.754	1.754	30	
1	3	3	1.698	1.695	10	
2	2	4 ⎫	1.614	1.624 ⎫	40	220
0	4	0 ⎭		1.603 ⎭		
2	3	3	1.549	1.546	40	
4	1	2	1.497	1.496	20	
2	4	0 ⎫	1.442	1.439 ⎫	10	
3	3	2 ⎭		1.488 ⎭		
2	4	2	1.374	1.374	70	311
0	4	4	1.311	1.316	30	222
2	2	6	1.278	1.276	20	
4	2	4	1.232	1.230	10	
3	4	3	1.190	1.189	10	
4	4	0	1.144	1.139	10	

[a] An additional line at $d = 2.87$ Å $(I = 30\%)$ was not indexed.

TABLE II. Calculated and observed powder pattern for Pr IV at 223 kbar. [a]

h	k	l	d_{obs}	d_{calc}	$I_{\text{obs}}(\%)$	Equivalent (hcp)
1	1	0	2.816	2.816	40	
0	0	2	2.482	2.481	50	002
2	0	0	2.431	2.438	100	100
1	0	2	2.209	2.211	80	
2	1	0	1.842	1.843	10	
2	0	2	1.738	1.739	70	102
3	0	1	1.550	1.545	5	
1	2	2	1.477	1.480	80	
2	2	0	1.406	1.408	40	110
2	2	1	1.354	1.354	30	
1	3	1	1.305	1.305	5	
1	0	4	1.203	1.202	50	

[a] An additional line at $d = 2.717$ Å $(I < 10\%)$ could not be indexed.
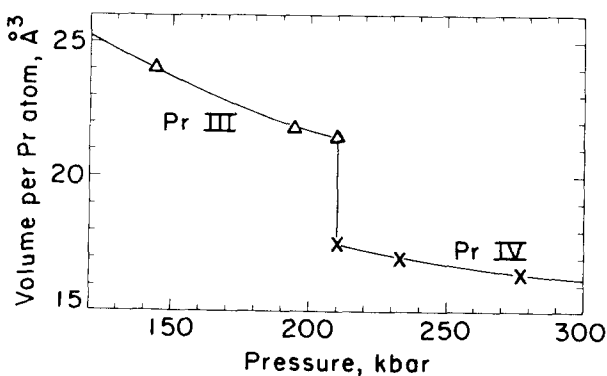

FIG. 2. Volume per Pr atom (Å³) for phases of praseodymium vs pressure.

Powder diffraction films of Pr IV above 210 kbar contained as many as 13 lines for which $\sin \theta /\lambda \leqslant 0.42$ (Table II). Four strong lines correspond in position and intensity to (002), (100), (102), and (110) reflections of an hcp structure with $a' \approx 2.8$ and $c' \approx 5.0$ Å. Additional reflections are an indication of a larger unit cell, probably a distorted hcp type. The Hesse-Lipson procedure[8] yielded a small hexagonal unit cell, with axes simply related the the hcp subcell: $a' \approx 2a'$ and $c \approx c'$. This Pr unit cell has four times the volume of the hcp subcell, or 8 atoms per unit cell, as illustrated in Fig. 1. It should be appreciated that derivation of this cell from x-ray powder diffraction data is not unique. This cell, however, has a high symmetry and a small lattice parameter and is an excellent fit to the data.

The space group of highest symmetry consistent with

TABLE III. Unit cell dimensions vs pressure for Pr II, III, and IV.

Pressure (kbar)	Phase	a(Å)	b(Å)	c(Å)	V(Å³)	V/atom (Å³)
69.2	II	4.820(2)	...	...	112.0(1)	28.0
144(4)	III	6.530(11)	6.412(8)	9.221(19)	386.2(7)	24.1
194(5)	III	6.334(11)	6.212(8)	8.852(18)	348.8(6)	21.8
212(3) { III		6.31(5)	6.19(3)	8.81(7)	343.9(22)	21.5
IV		5.678(5)	...	5.017(6)	140.1(3)	17.5
233(8)	IV	5.632(3)	...	4.962(5)	136.3(2)	17.0
277(10)	IV	5.570(4)	...	4.912(s)	132.2(2)	16.5

the observed unit cell and assumed distorted hcp topology is trigonal, $P\,3m1$. The site symmetry of Pr atoms in Pr IV has been reduced from $6m2$ in ideal hcp to no greater than $3m$ or m in the trigonal phase. The atomic volume, for $Z = 8$, is less than 17.5 Å³ per Pr, as illustrated in Fig. 2.

Unit cell data points for Pr III and Pr IV at pressure, recorded in Table III, are illustrated in terms of volume per atom in Fig. 2. In the experiment at 212 kbar Pr III and Pr IV coexist. The large relative volume change at the transition, calculated to be 19%, exceeds the one in cerium.[9]

In contrast to the isostructural transition in Ce, the Pr transition is accompanied by a change of symmetry; because both Pr III and Pr IV are distorted, essentially twelve-fold coordinated, close-packed structures, however, the observed volume collapse is attributed mainly to a collapse of the metallic radius, in close analogy with Ce.

In summary, the present experiments provide strong evidence for the hypothesis[2] that the Pr III–IV transition is the $4f^2$ counterpart of the $4f^1$ delocalization transition in Ce. It may be fruitful to investigate the other light rare-earth metals for similar $4f$-shell delocalizations up to pressures in the megabar range.[5] In a recent band structure calculation for americium, Skriver et al.[10] predicted a volume collapse at $\simeq 100$ kbar that they attributed to a delocalization of a similar volume collapse at 30 kbar.[11] Hence, there is some theoretical support for our interpretation, although the rather poor quantitative agreement for the transition pressure raises questions concerning its applicability.

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[2] J. Wittig, Z. Phys. B **38**, 11 (1980).
[3] We call the phase of Pr which is stable between $\simeq 75$ and 212 kbar Pr III.
[4] See Ref. 2 for a list of references to recent work on cerium.
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