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THE CRYSTAL STRUCTURES OF CERIUM METAL AT HIGH PRESSURE

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W. H. Zachariasen and F. H. Ellinger

ABSTRACT

The high pressure form of cerium metal stable above 51 kbar, α' -Ce, is found to be orthorhombic with the α -U type of structure. At 58 kbar the cell dimensions of α' -Ce are: $a = 3.049 \text{ \AA}$, $b = 5.998 \text{ \AA}$, $c = 5.215 \text{ \AA}$. A second, metastable phase of cerium metal, α'' -Ce, has also been observed. It is monoclinic body-centered with a deformed, face-centered cubic (fcc) structure. The cell dimensions of α'' -Ce at 56 kbar are: $a = 4.762 \text{ \AA}$, $b = 3.170 \text{ \AA}$, $c = 3.169 \text{ \AA}$, $\beta = 91.73^\circ$. The volume change at the α - α' transition point is $\Delta V/V = 0.011$. Cerium metal is fully tetravalent in both α' -Ce and α'' -Ce.

I. INTRODUCTION

This report describes the results of *in situ* x-ray diffraction studies of cerium metal at pressures up to ~100 kbar. All observations were made at room temperature. A preliminary report of our findings was published two years ago.¹

The form of cerium metal at room pressure and temperature, γ -Ce, as shown by Lawson and Tang,² is transformed into α -Ce at ~8 kbar. This transformation is of unique type: both phases have the fcc structure, but the volume reduction is unusually large, $\Delta V/V = 0.148 \pm 0.003$. Zachariasen suggested that this volume collapse was due to electron promotion from the 4f to the valence shell.³

A number of investigators have observed a second phase transformation $\alpha \rightarrow \alpha'$ in cerium metal. The transformation pressure has been reported to be 91 kbar by Bridgman,⁴ 60 to 65 kbar by Stager and Drickamer,⁵ 50 kbar by Wittig,⁶ 56 kbar by King et al.,⁷ and 51 kbar by Schaufelberger and Merx.⁸ Wittig reported that α' -Ce becomes superconducting below 1.7 K.

According to Franceschi and Olcese,⁹ α' -Ce has the fcc structure with a unit cell edge $a = 4.66 \pm 0.01 \text{ \AA}$ which remains unchanged from 50 to 80 kbar. McWhan,¹⁰ on the other hand, found that α' -Ce has

the hexagonal close-packed (hcp) structure with cell constants $a = 3.16 \pm 0.01 \text{ \AA}$, $c = 5.20 \pm 0.02 \text{ \AA}$ at ~65 kbar. Our preliminary publication¹ reports the existence of two high pressure phases, α' -Ce and α'' -Ce. α' -Ce was found to have the α -U type of structure, whereas α'' -Ce was found to be monoclinic body-centered with just two atoms per unit cell. The cell constants were reported to be:

α' -Ce at 66 kbar:

$$a = 3.06 \pm 0.01 \text{ \AA}$$

$$b = 6.01 \pm 0.01 \text{ \AA}$$

$$c = 5.23 \pm 0.01 \text{ \AA}$$

α'' -Ce at 56 kbar:

$$a = 4.79 \pm 0.02 \text{ \AA}$$

$$b = 3.20 \pm 0.01 \text{ \AA}$$

$$c = 3.18 \pm 0.01 \text{ \AA}$$

$$\beta = 92.1 \pm 0.2^\circ$$

Schaufelberger and Merx⁸ state that α' -Ce is a mixture of isodensity fcc and hcp phases and possibly a third, metastable component.

In view of the conflicting findings of the various investigators it seems necessary to present the interpretation of our x-ray diffraction data in some detail.

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II. EXPERIMENTAL PROCEDURE

The diffraction patterns of cerium metal were obtained with diamond-anvil equipment of the type described by Bassett, Takahashi, and Stook,¹¹ using filtered MoK α radiation. The beam incident upon the sample had a diameter of 100 μ , and the pressure gradient in the irradiated part of the specimen was negligible. Because of the transmission method used in the experiments, absorption increased rapidly with scattering angle, and it was rarely possible to measure diffraction lines beyond $2\theta = 40^\circ$.

With our equipment it was difficult to measure the pressures at which the diffraction patterns were taken. Indeed, the pressures given in Ref. 1 are too high by 10 to 12 kbar. In this report it will be assumed that the α - α' transition occurs at 51 ± 1 kbar as found by Schaufelberger and Merx, and further that the lattice constant of α -Ce in the range 18 to 51 kbar varies with pressure as found by these investigators. For pressures above 51 kbar we have assumed that the atomic volume of α' -Ce is 23.91 $\text{\AA}^3$ at 56 kbar, 22.52 $\text{\AA}^3$ at 100 kbar, and that the compressibility of α' -Ce is constant. The resulting pressure calibration in terms of the atomic volumes of α -Ce and α' -Ce is shown in Table I. According to this table, Franceschi and Olcese's experiments were carried out at effective pressure not exceeding 35 kbar, i.e., well below the α - α' transition.

Six different samples of cerium metal were used in the investigation; four of them were slices cut from the same piece of U. S. Bureau of Mines high-purity electrolytic metal. More than 90 x-ray diffraction patterns were taken in the course of the study. Diffraction data are given in the tables as $S \equiv 10^4 \sin^2\theta$ with intensities listed as very strong (vs), strong (s), medium (m), weak (w), very weak (vw), trace (t); the symbol D indicates a diffuse or unresolved double line. Except for very weak diffraction lines the maximum error in measured S-values is ± 1 for $S = 100$ and ± 3 for $S = 1000$.

Attempts to interpret the diffraction patterns were unsuccessful until it was demonstrated experimentally that nearly all patterns taken at pressures above 51 kbar were due to a mixture of two high pressure phases, α' -Ce and α'' -Ce. When the specimen was subjected to pressure cyclings some of the lines of the diffraction pattern became spotty while others remained smooth; as the cyclings proceeded the spotty lines gained in intensity while the smooth lines became weaker. Accordingly, one high pressure phase, α' -Ce, associated with the spotty diffraction lines, showed appreciable crystal growth induced by the cycling process, while the se-

cond phase, α'' -Ce, responsible for the smooth lines, showed no noticeable increase in crystallite size.

Large hysteresis effects were observed. Thus, samples which had been subjected to high pressures showed the presence of the high pressure phases together with the α -phase in diffraction patterns taken at pressures as low as 27 kbar.

III. THE STRUCTURE OF α' -Ce

Table II compares diffraction data for two of our patterns and the one observed by McWhan. Pattern A was taken at a pressure of 82 kbar, the pressure having been increased to this value in steps. All the diffraction lines of pattern A were smooth. Pattern B was taken of the same specimen at a pressure of 58 kbar after many pressure cyclings. All the diffraction lines, except for the two very weak ones given in parentheses, became spotty and had to be ascribed to the coarsely crystalline α' -phase which, clearly, is the same phase that McWhan reported.

McWhan's proposed hexagonal indexing is not acceptable: (1) Some of the lines of pattern B cannot be explained. (2) One of the strongest reflections, (112), of the hcp structure with all atoms scattering in phase is not even observed. (3) Lines $S = 171$ and $S = 500$ correspond to the hexagonal reflection (100) and (110) with S-values in the ratio 1:3.00, whereas the measured ratio is $1:2.93 \pm 0.02$.

However, as demonstrated in Tables II and III, all diffraction lines of the α' -Ce patterns can be satisfactorily explained in terms of a C-centered orthorhombic unit cell. Cell dimensions as deduced from the data of Table II are:

Pattern A:

$$\begin{aligned}a &= 3.009 \pm 0.005 \text{ \AA} \\b &= 5.918 \pm 0.010 \text{ \AA} \\c &= 5.145 \pm 0.010 \text{ \AA}\end{aligned}$$

Pattern B:

$$\begin{aligned}a &= 3.049 \pm 0.005 \text{ \AA} \\b &= 5.988 \pm 0.010 \text{ \AA} \\c &= 5.215 \pm 0.010 \text{ \AA}\end{aligned}$$

Cell dimensions as deduced from the data of Table III are:

α -Ce:

$$a = 4.677 \pm 0.004 \text{ \AA}$$

α' -Ce:

$$\begin{aligned}a &= 3.110 \pm 0.005 \text{ \AA} \\b &= 6.061 \pm 0.010 \text{ \AA} \\c &= 5.274 \pm 0.010 \text{ \AA}\end{aligned}$$

TABLE I
VARIATION OF ATOMIC VOLUME WITH PRESSURE^a

P (kbar)	γ -Ce		α -Ce		α'' -Ce
	a (Å)	V (Å ³)	a (Å)	V (Å ³)	V (Å ³)
0	5.164	34.43	(4.877	29.00)	(26.26)
4.5	5.104	33.24	4.831	28.19	---
7.5	5.063	32.45	4.800	27.65	---
10	---	---	4.780	27.30	---
20	---	---	4.714	26.19	---
30	---	---	4.665	25.38	---
40	---	---	4.631	24.83	---
50	---	---	4.604	24.40	---
51	---	---	4.602	24.37	24.10
56	---	---	---	---	[23.91]
60	---	---	---	---	23.76
70	---	---	---	---	23.36
80	---	---	---	---	22.98
90	---	---	---	---	22.60
100	---	---	---	---	[22.22]

^aNumbers given in parentheses are extrapolated values. Numbers given in brackets are experimental values (see Sec. II).

The observed volume and intensities require four cerium atoms per unit cell in positions 4c of the space group Cmc₂m. These positions are (000) (1/2 1/2 0) + : ± (0y 1/4) with y ≈ 1/10. It was realized at this stage that the structure deduced for α' -Ce is of the α -U type first described by Jacob and Warren.¹² In fact, it is the first known example of this structure type other than uranium itself.

Our data do not permit a precise determination of the parameter y, hence we will assume that it has the same value y = 0.105 as found by Jacob and Warren for the α -U structure, however the accuracy is no better than y = 0.105 ± 0.010.

Calculated and observed intensities for α -U and α' -Ce are shown in Table IV. The calculated intensities are given as $I \propto |F/f|^2 p$ where p is the multiplicity. Since all angle-dependent factors are omitted, only neighboring reflections should be compared. There is evidence of some preferential orientation: reflections with small values of the index L appear with enhanced intensity, indicating that the orthorhombic c-axis tends to align with the incident beam which has the direction of maximum pressure.

Bond lengths in α' -Ce at 58 kbar are:

Ce-2Ce	2.90 ± 0.05 Å
-2Ce	3.05 ± 0.01 Å
-4Ce	3.36 ± 0.01 Å
-4Ce	3.49 ± 0.06 Å

The bond angle for the two shortest bonds is 128 ± 5°, and endless zig-zag chains of cerium atoms are formed in the c-direction. The bond angle for the two next-shortest bonds is 180°, corresponding to endless straight chains along the a-axis.

IV. THE CRYSTAL STRUCTURE OF α'' -Ce

The diffraction pattern of α'' -Ce is quite similar to that of α -Ce, except that the fcc diffraction lines have been split into components. This close relationship is demonstrated in Table V which presents the data from a diffraction pattern taken at 41 kbar. This diffraction pattern shows the presence of both α -Ce and α'' -Ce. Also shown in Table V are the data from a single phase diffraction pattern of α'' -Ce taken at 90 kbar.

The diffraction lines of α'' -Ce correspond to a pseudo-cubic monoclinic body-centered structure with only two atoms per unit cell, as demonstrated by the indexings shown in Table V. Cell dimensions deduced from the data of Table V are:

41 kbar pattern
α'' -Ce:
a = 4.629 ± 0.006 Å
V = 24.80 Å ³

TABLE II

DIFFRACTION DATA FOR α' -Ce

HKL	Pattern A (82 kbar)			Pattern B (58 kbar)			McWhan	
	S _{calc}	I _{obs}	S _{obs}	S _{calc}	I _{obs}	S _{obs}	I _{obs}	S _{obs}
020	144	vw	146	140	vw	138	---	---
110	176	vs	175	171	s	171	m	170
---	---	---	---	---	(vw	182)	---	---
002	191	vsD	192 ^a	186	m	187	s	186
021	192			187				
111	223	s	223 ^a	217	s	217	m	217
---	---	wm	263 ^b	---	(vw	252)	---	---
022	335	---	---	326	t	330	---	---
112	366	m	366	357	m	357	vw	355
130	464	---	---	452	---	---	---	---
---	---	vw	471 ^b	---	---	---	---	---
131	512	sD	513 ^a	498	s	500	m	499
200	558	w	557	543	vw	542	---	---
023	574	vw	578	558	---	---	---	---
040	577			562	---	---	---	---
113	605	---	---	589	vw	589	---	---
041	625	vwD	625 ^a	608	---	---	---	---
132	655	---	---	638	vw	637	---	---
220	702	---	---	684	---	---	---	---
---	---	vwD	717 ^b	---	---	---	---	---
202	749	mD	749 ^a	729	m	729	w	725
221	750			730				
004	763	---	---	743	---	---	vw	748
042	768	---	---	747	---	---		
222	893	---	---	869	---	---	---	---
133	893	vw	897	870	m	868	t	870
024	907	---	---	883	---	---	---	---
114	939	vw	942	914	---	---	---	---
043	1006	---	---	980	---	---	---	---
150	1041	vw	1040	1013	vw	1010	t	1014
151	1089	---	---	1060	---	---	---	---
223	1132	vw	1134	1102	m	1106	t	1103
240	1135			1105				
241	1183	---	---	1151	---	---	---	---
134	1227	vw	1233	1195	w	1197	t	1207
152	1232			1199				
310	1292	vw	1293	1257	w	1268	---	---
060	1298			1264				

^a Coincidence with prominent lines of α'' -Ce.^b Diffraction lines of α'' -Ce. α'' -Ce:

$$a = 4.806 \pm 0.012 \text{ \AA}$$

$$b = 3.194 \pm 0.006 \text{ \AA}$$

$$c = 3.196 \pm 0.006 \text{ \AA}$$

$$\beta = 92.18 \pm 0.40^\circ$$

$$V = 24.51 \text{ \AA}^3$$

$$a:b:c = 1.508:1:1.001$$

90 kbar pattern

 α'' -Ce:

$$a = 4.702 \pm 0.010 \text{ \AA}$$

$$b = 3.102 \pm 0.005 \text{ \AA}$$

$$c = 3.104 \pm 0.005 \text{ \AA}$$

$$\beta = 91.99 \pm 0.20^\circ$$

$$V = 22.62 \text{ \AA}^3$$

$$a:b:c = 1.516:1:1.001$$

Were $\beta = 90^\circ$ and the axial ratios $\sqrt{2}:1:1$, the monoclinic structure would become the fcc structure.

TABLE III

DIFFRACTION DATA FOR α -Ce + α' -Ce AT 27 kbar

I_{obs}	S_{obs}	α -Ce		α' -Ce	
		HKL	S_{calc}	HKL	S_{calc}
vw	138	---	---	020	138
s	165	---	---	110	165
m	175	111	173	---	---
s	183	---	---	002	182
s	209	---	---	021	183
wm	231	200	231	111	210
vw	248 ^a	---	---	---	---
m	347	---	---	112	347
w	460	220	462	---	---
ms	486	---	---	131	485
vw	518	---	---	200	522
vw	545	---	---	023	546
vw	592	---	---	040	550
wm	634	311	635	041	595
mD	703	222	693	---	---
w	847	---	---	202	704
w	995	---	---	221	705
vw	1074	---	---	133	849
vw	1168	---	---	150	990
				240	1072
				223	1069
				152	1172

^a(011) reflection from α'' -Ce.

Diffraction patterns of cerium metal taken at 56 kbar and at 100 kbar have been published by Schaufelberger and Merx.⁸ Detailed analysis of their data shows that the bulk of their sample is α'' -Ce. Table VI gives the S-values, obtained from their published 2θ -values, for all lines due to the α'' -phase (up to $S = 1064$). The agreement between observed and calculated S-values is excellent. The unit cell dimensions deduced from their patterns are:

56 kbar pattern

$$\begin{aligned} a &= 4.762 \pm 0.006 \text{ \AA} \\ b &= 3.170 \pm 0.005 \text{ \AA} \\ c &= 3.169 \pm 0.005 \text{ \AA} \\ \beta &= 91.73 \pm 0.15^\circ \\ V &= 23.91 \text{ \AA}^3 \end{aligned}$$

100 kbar pattern

$$\begin{aligned} a &= 4.686 \pm 0.006 \text{ \AA} \\ b &= 3.073 \pm 0.005 \text{ \AA} \\ c &= 3.089 \pm 0.005 \text{ \AA} \\ \beta &= 92.69 \pm 0.15^\circ \\ V &= 22.22 \text{ \AA}^3 \end{aligned}$$

Below is a list of diffraction lines reported by Schaufelberger and Merx which we have never observed and which remain unexplained.

56 kbar pattern			100 kbar pattern		
Line No.	I_{obs}	S_{obs}	Line No.	I_{obs}	S_{obs}
4*	w	268	4*	m	308
5*	w	294	5*	vw	385
6	vw	387	6*	w	409
7	vw	396	7*	w	421
			8	w	455
17	vw	803	18	vw	837
			19	vw	845
18	vw	847	20	vw	892
20	m	920	22	w	969

The lines marked by asterisks were attributed by Schaufelberger and Merx to extraneous, but unidentified, material in the pressure cell.

Since the positions of the two atoms in the α'' -Ce structure are $(000)(1/2 \ 1/2 \ 1/2)$, the calculated intensities are directly proportional to the multiplicity p . In Table VII the values of p and the observed intensities are compared. As in α' -Ce there is evidence of preferred orientation. For five of our six samples and the two patterns of Schaufelberger and Merx, the intensity of a reflection (HKL) is enhanced relative to the companion reflection (HKL). This indicates a tendency of the plane $(10\bar{1})$ to line up normal to the incident beam. However, in our sixth sample, 17709, the (HKL) component is enhanced, indicating a tendency of the (101) plane to be oriented normal to the incident beam.

Bond lengths in the α'' -Ce structure at 56 kbar are:

Ce-2Ce	$3.169 \pm 0.005 \text{ \AA}$
-2Ce	$3.170 \pm 0.05 \text{ \AA}$
-4Ce	$3.235 \pm 0.010 \text{ \AA}$
-4Ce	$3.305 \pm 0.010 \text{ \AA}$

Thus, as in α' -Ce, there are four short and eight longer bonds. The short bonds form endless straight chains along the b-axis and along the c-axis.

V DISCUSSION

The variation of unit cell dimensions of α'' -Ce and α' -Ce with pressure is given in Table VIII. The two high pressure phases have the same volume within

TABLE IV
INTENSITIES FOR α -U AND α' -Ce

HKL	I_{calc}	I_{obs}		HKL	I_{calc}	I_{obs}	
		α -U	α' -Ce			α -U	α' -Ce
020	0.2	vw	vw	202	8.0	s	m
110	5.0	s	s	221	15.0		
002	4.0	s	m	004	4.0		
001	7.5	s		042	6.1	m	vw
111	6.0	s	s	222	1.0	vw	m
022	0.5	vw	t	133	13.5		
112	10.0	s	m	024	0.5	vw	---
130	1.3	vw	---	114	10.0	m	vw
131	13.5	s	s	043	1.9	vw	---
200	4.0	w	vw	150	7.8	wm	vw
023	7.5	m	vw	151	0.4	nil	---
040	3.1	w		223	15.0	m	m
113	6.0	m	vw	240	6.1	w	
041	1.9	vw	vw	241	3.7	vw	---
132	2.5	w	vw	134	2.5	vw	w
202	0.5	vw	---	152	15.6		

TABLE V
DIFFRACTION DATA FOR α -Ce + α'' -Ce AT 41 kbar AND FOR

α		α''		$\alpha + \alpha''$ (41 kbar)		α'' (90 kbar)		
HKL	S_{calc}	HKL	S_{calc}	I	S_{obs}	S_{calc}	I	S_{obs}
111	177	101	172	vw	172	182	vw	180
		110	179	vs	177	188	vs	188
		101	185			194		
200	236	200	219	m	219	229	w	227
		---	---	w	237	---	---	---
		011	248	m	248	262	vs	262
220	471	211	454	w	454	479	w-	479
		211	479	m	474	505	w+	505
		020	495	w	495	525	w-	525
		002	495			525		
		301	598			628	---	---
311	648	310	617	wD	609	646	w	646
		301	635	wD	647	664	---	---
		112	661			701	w	703
		121	667			707		
		121	680			719		
222	707	112	686	wD	680	725	w	721
		202	689	---	---	730	---	---
		220	714			754	w	755
		202	739			778	---	---

TABLE VI
INTERPRETATION OF THE DIFFRACTION DATA
REPORTED BY SCHAUFELBERGER AND MERX

HKL	56 kbar			100 kbar		
	<u>S_{calc}</u>	<u>I_{obs}</u>	<u>S_{obs}</u>	<u>S_{calc}</u>	<u>I_{obs}</u>	<u>S_{obs}</u>
10 $\bar{1}$	177	vs	181	182	---	---
110	181			192	vs	192
101	187			198	vs	198
200	223	m	222	231	w	231 ^a
011	252	s	252	267	vs	267
21 $\bar{1}$	464	w	464	481	vw	484
211	485	m	486	513	s	514
002	503	s	502	530	s	532
020	503			536		
30 $\bar{1}$	612	---	---	627	---	---
310	627	w	627	653	w	653
301	643	w	641	676	w	679
11 $\bar{2}$	675	s	679	706	---	---
121	679			718	s	719
121	689	s	689	734	vs	736
11 $\bar{2}$	695			738		
202	706	---	---	729	w	764
220	726	m	727	767		
202	747	vw	747	793	w	792
400	892	w	893	922	vw	922
022	1006	w	1005	1066	m	1064

^aThis diffraction line occurs at $2\theta = 17.49^\circ$ according to the published patterns,⁸ but was omitted from the list of reflections given by Schaufelberger and Merx.

experimental error. However, there is a small volume change (of $\sim \Delta V/V = 0.011$) when the α -phase is transformed to the α' - or α'' -phase.

Nearly all of the diffraction patterns taken at pressures above 51 kbar show the presence of both α' -Ce and α'' -Ce. However, the transition α'' -Ce to α' -Ce proceeds at a very slow rate under constant pressure. Thus, one specimen was held at a pressure of 95 kbar for 10 days without a measurable change in the relative proportion of the two phases. Pressure cycling does, however, induce the $\alpha'' \rightarrow \alpha'$ transition. This observation is the only basis for our conclusion that the α' -phase is the stable form and the α'' -phase the metastable form of cerium metal at high pressures. The only single-phase diffraction patterns of α'' -Ce were obtained when the pressure was raised in one quick step from its room value to 90 or 96 kbar. It is probable that a very slow rate of pressure increase near the transformation point will favor the formation of α' -Ce.

The transformation $\alpha \rightarrow \alpha''$ involves only small shifts in the relative atomic positions ($\sim 0.1 \text{ \AA}$) so

that a single crystallite of α -Ce should be transformed into a single crystallite of α'' -Ce. The $\alpha \rightarrow \alpha'$, or $\alpha'' \rightarrow \alpha'$ transformation, on the other hand, involves a major structural reorganization. The $\alpha \rightarrow \alpha''$ phase change can probably be characterized as a second order transformation, but there is, as mentioned above, a small, discontinuous volume change.

The observed variation of atomic volume with pressure for α -Ce is shown in Table I and Fig. 1. Analysis of the data shows a rapid decrease in the value of the compressibility K from 7.5 to 51 kbar, and hence also in the extrapolated value of atomic volume V_0 at zero pressure. Results of this analysis are shown in Table IX. The same value $K = 1.7 \times 10^{-3}/\text{kbar}$ is obtained for α -Ce in the range 40 to 51 kbar, for α' -Ce in the range 58 to 95 kbar, and for α'' -Ce in the range 56 to 100 kbar.

It is convenient to define the metallic radius R for 12 coordination in terms of the atomic volume per atom V by the equation¹³

$$R \equiv (V^{1/3})/(2^{5/6}).$$

TABLE VII
 α'' -Ce INTENSITIES

HKL	Multi- plicity	I _{obs}			
		90 kbar Pattern of Table V	56 kbar Pattern of Table VI	100 kbar Pattern of Table VI	65 kbar Pattern of Specimen 17709a
10 $\bar{1}$	2	vw		---	s ^b
110	4	vs	vs	vs	s ^b
101	2			vs	s ^b
200	2	w	m	w	s ^b
01 $\bar{1}$	4	vs	s	vs	m
21 $\bar{1}$	4	w-	w	vw	m
211	4	w+	m	s	m
002	2	w-	s	s	vw+
020	2				
301	2	---	---	---	w+
310	4	w	w	w	w+
30 $\bar{1}$	2	---	w	w	---
11 $\bar{2}$	4	w	s	---	vw
12 $\bar{1}$	4			s	
121	4				
112	4	w	s	vs	wD
20 $\bar{2}$	2				
220	4	w	m	w	vw+
202	2	---	vw	w	---
400	2	---	w	vw	w
022	4	---	w	m	vw

^aWith unusual preferred orientation effect.

^bCoincidence with α' -Ce lines.

Pauling¹⁴ was the first to point out that the metallic radius of cerium in γ -Ce is smaller than expected from a comparison with typically trivalent 4f metals, and he suggested a metallic valence $v = 3.2$ for cerium in γ -Ce. The expected value for the metallic radius of cerium for $v = 3.00$ is $R = 1.851 \text{ \AA}$. On the other hand, when cerium is fully tetravalent, i.e., a member of the series of d-elements Ti-Zr-Ce-Th, the estimated metallic radius is $1.672 \text{ \AA}$.¹⁵ Table IX shows that the metallic radius of cerium of all three phases, α , α' , and α'' , extrapolated to room pressure from 50 kbar and above, agrees with the predicted value for $v = 4.00$. Indeed, the small value for the compressibility of $K = 1.7 \times 10^{-3}/\text{kbar}$, observed for pressures above 50 kbar, also indicates full tetravalency for cerium.

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TABLE VIII

UNIT CELL DIMENSIONS FOR α' -Ce AND α'' -Ce^a

α' -Ce						Second Phase	
P (kbar)	a (Å)	b (Å)	c (Å)	β (deg)	V (Å ³)	Phase	V (Å ³)
27	3.110(5)	6.061(10)	5.274(10)	---	24.85	α	25.60
49	3.081(5)	5.995(10)	5.225(10)	---	24.13	α	24.46
58	3.049(5)	5.998(10)	5.215(10)	---	23.84	α''	---
65	3.036(5)	5.956(10)	5.183(10)	---	23.43	α''	23.55
82	3.009(5)	5.918(10)	5.145(10)	---	22.90	α''	22.87
95	2.993(5)	5.868(10)	5.103(10)	---	22.40	α''	22.46

α'' -Ce						Second Phase	
P (kbar)	a (Å)	b (Å)	c (Å)	β (deg)	V (Å ³)	Phase	V (Å ³)
39	4.815(12)	3.204(6)	3.205(6)	91.23(40)	24.71	α	24.88
41	4.806(12)	3.194(6)	3.196(6)	92.18(40)	24.51	α	24.80
56	4.762(6)	3.170(5)	3.169(5)	91.73(15)	23.91	---	---
65	4.773(10)	3.114(6)	3.172(6)	92.33(20)	23.55	α'	23.43
82	4.762(15)	3.099(6)	3.102(6)	92.51(40)	22.87	α'	22.90
87	4.732(12)	3.099(6)	3.102(6)	92.49(30)	22.72	α'	---
90	4.702(10)	3.102(5)	3.104(5)	91.99(20)	22.62	---	---
95	4.733(15)	3.081(6)	3.084(6)	92.64(40)	22.46	α'	22.40
96	4.685(12)	3.090(6)	3.092(5)	91.97(30)	22.37	---	---
100	4.686(6)	3.073(5)	3.089(5)	92.69(15)	22.22	---	---

^a Estimated error in last decimal place given in parentheses.

Fig. 1.

Atomic volumes observed for α -Ce, α' -Ce, α'' -Ce.6. J. Wittig, "Superconductivity of Cerium under Pressure," Phys. Rev. Lett. **21**, 1250-1252 (1968).7. E. King, J. A. Lee, I. R. Harris, and T. F. Smith, "New Phase Boundary for Cerium," Phys. Rev. **B1**, 1380-1381 (1970).

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TABLE IX

VARIOUS PROPERTIES OF THE METAL PHASES

<u>Phase</u>	<u>P (kbar)</u>	<u>K (10^{-3}/kbar)</u>	<u>$V_0 (\text{\AA}^3)$</u>	<u>R ($\text{\AA}$)</u>	<u>v</u>
Ideal	0	---	35.89	1.851	3.00
γ -Ce	0	---	34.43	1.825	3.15
α -Ce	0	---	29.00	1.724	3.72
α -Ce	7.5- 25	4.1	28.52	1.714	3.77
α -Ce	25 - 40	2.3	27.27	1.689	3.90
α -Ce	40 - 51	1.7	26.58	1.675	3.97
α' -Ce	58 - 95	1.7	26.29	1.669	4.00
α'' -Ce	56 -100	1.7	26.26	1.668	4.00

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