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The Crystal Structures of Cerium Metal at High Pressure*

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The high-pressure form of cerium metal stable above 51 kbar, α′-Ce, is found to be orthorhombic with the α-uranium type of structure. At 58 kbar the cell dimensions of α′-Ce are $a=3{\cdot}049$, $b=5{\cdot}998$, $c=5{\cdot}215$ Å. A second, metastable, phase of cerium metal, α″-Ce, has also been observed. It is monoclinic body-centered with a deformed cubic face-centered structure. The cell dimensions of α″-Ce at 56 kbar are $a=4{\cdot}762$, $b=3{\cdot}170$, $c=3{\cdot}169$ Å, $\beta=91{\cdot}73°$. The volume change at the α–α′ transition point is $\Delta V/V=0{\cdot}011$. Cerium metal is fully tetravalent in both α′-Ce and α″-Ce.

1. Introduction

This paper describes the results of *in situ* X-ray diffraction studies of cerium metal at pressures up to about 100 kbar. All observations were made at room temperature. A preliminary report of our findings was published two years ago (Ellinger & Zachariasen, 1974).

The room pressure and room temperature form of cerium metal, γ-Ce, is transformed into α-Ce (Lawson & Tang, 1949) at about 8 kbar. This transformation is of unique type: both phases have the f.c.c. structure, but the volume reduction is unusually large, $\Delta V/V=0{\cdot}148\pm0{\cdot}003$. It was suggested (Zachariasen, 1949) that this volume collapse was due to electron promotion from the $4f$ to the valence shell.

A number of investigators have observed a second phase transformation $\alpha \rightleftarrows \alpha'$ in cerium metal. The transformation pressure has been reported to be 91 (Bridgman, 1952), 60–65 (Stager & Drickamer, 1964), 50 (Wittig, 1968), 56 (King, Lee, Harris & Smith, 1970) and 51 kbar (Schaufelberger & Merx, 1974). Wittig reported that α′-Ce becomes superconducting below 1·7 K.

According to Franceschi & Olcese (1969) α′-Ce has the f.c.c. structure with a unit-cell edge $a=4{\cdot}66\pm0{\cdot}01$ Å which remains unchanged from 50 to 80 kbar. McWhan (1970), on the other hand, found that α′-Ce has the h.c.p. structure with cell constants $a=3{\cdot}16\pm0{\cdot}01$, $c=5{\cdot}20\pm0{\cdot}02$ Å at about 65 kbar. In our preliminary publication the existence of two high-pressure phases, α′-Ce and α″-Ce, was reported. α′-Ce was found to have the α-uranium type of structure, while α″-Ce was found to be monoclinic body-centered with just two atoms per unit cell. The cell constants were reported to be for α′-Ce at 66 kbar: $a=3{\cdot}06\pm0{\cdot}01$, $b=6{\cdot}01\pm0{\cdot}01$, $c=5{\cdot}23\pm0{\cdot}01$ Å; and for α″-Ce at 56 kbar: $a=4{\cdot}79\pm0{\cdot}02$, $b=3{\cdot}20\pm0{\cdot}01$, $c=3{\cdot}18\pm0{\cdot}01$ Å, $\beta=92{\cdot}1\pm0{\cdot}2°$.

Schaufelberger & Merx (1974) state that α′-Ce is a mixture of f.c.c. and h.c.p. phases of equal density 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.

2. Experimental

The diffraction patterns were obtained with diamond-anvil equipment of the type described by Bassett, Takahashi & Stook (1967), using filtered Mo $K\alpha$ radiation. The beam incident upon the sample had a diameter of 100 μm, and the pressure gradient in the irradiated part of the specimen was negligible. Because of the transmission method used in the experiments the absorption increased rapidly with scattering angle, and it was rarely possible to measure diffraction lines beyond $2\theta=40°$.

It was difficult with our equipment to measure the pressures at which the diffraction patterns were taken. Indeed, the pressures given in our preliminary publica-

Table 1. *Variation of atomic volume with pressure*

	γ-Ce		α-Ce		α″-Ce
P (kbar)	a (Å)	V (Å³)	a (Å)	V (Å³)	V (Å³)
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]

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tion are too high by 10–12 kbar. In this paper it will be assumed that the α–α' transition occurs at 51 ± 1 kbar as found by Schaufelberger & Merx (1974), and further that the lattice constant of α-Ce in the range 18–51 kbar varies with pressure as found by these workers. For pressures above 51 kbar it will be assumed that the atomic volume of α''-Ce is 23·91 Å^3 at 56 kbar, 22·22 Å^3 at 100 kbar and that the compressibility of α''-Ce is constant. These atomic volumes were deduced from our interpretation of the diffraction data at 56 and 100 kbar published by Schaufelberger & Merx (1974). The resulting pressure calibration in terms of the atomic volumes of α-Ce and α''-Ce is shown in Table 1. According to this table Franceschi & Olcese's experiments were carried out at an 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 US Bureau of Mines high-purity electrolytic metal. More than 90 X-ray diffraction patterns were taken in the course of the study. The diffraction data will be given 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*), while the symbol *D* is used to indicate 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 those of 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, and 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 second phase, α''-Ce, responsible for

Table 2. *Diffraction data for* α'-Ce

	Pattern *A* 82 kbar			Pattern *B* 58 kbar			McWhan (1970)	
HKL	S_{cal}	I_{obs}	S_{obs}	S_{cal}	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*	186	*m*	187	*s*	186
021	192			187				
111	223	*s*	223*	217	*s*	217	*m*	217
		wm	263†		(*vw*	252)		
022	335			326	*t*	330		
112	366	*m*	366	357	*m*	357	*vw*	355
130	464			452				
		vw	471†					
131	512	*sD*	513*	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*	608				
132	655			638	*vw*	637		
220	702			684				
		vwD	717†					
202	749	*mD*	749*	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				

* Coincidence with prominent lines of α''-Ce.
† Diffraction lines of α''-Ce.

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.

3. The structure of α′-Ce

Table 2 shows the diffraction data for two of our patterns and for the pattern observed by McWhan (1970). 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* are 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, have become spotty and must be ascribed to the coarsely crystalline α′-phase, which clearly is the same phase that McWhan reported.

The proposed hexagonal indexing is not acceptable because (1) some of the lines of pattern *B* cannot be explained, (2) one of the strongest reflections, 112, of the h.c.p. structure with all atoms scattering in phase is not even observed, (3) the lines $S=171$ and $S=500$ correspond to the hexagonal reflections 100 and 110 with *S* values in the ratio 1:3·00, while the measured ratio is $1:2{\cdot}93\pm0{\cdot}02$.

However, as demonstrated in Tables 2 and 3 all the diffraction lines of the α′-Ce patterns can be satisfactorily explained in terms of a *C*-centered orthorhombic unit cell. The cell dimensions as deduced from the data of the tables are from Table 2, Pattern *A*: $a=3{\cdot}009\pm0{\cdot}005$, $b=5{\cdot}918\pm0{\cdot}010$, $c=5{\cdot}145\pm0{\cdot}010$; Pattern *B*: $a=3{\cdot}049\pm0{\cdot}005$, $b=5{\cdot}988\pm0{\cdot}010$, $c=5{\cdot}215\pm0{\cdot}010$ Å; from Table 3, α-Ce: $a=4{\cdot}677\pm0{\cdot}004$; α′-Ce: $a=3{\cdot}110\pm0{\cdot}005$, $b=6{\cdot}061\pm0{\cdot}010$, $c=5{\cdot}274\pm0{\cdot}010$ Å.

The observed volume and the observed intensities require four Ce atoms per unit cell in the positions 4(*c*) of the space group *Cmcm*. These positions are $(000)\,(\frac{1}{2}\frac{1}{2}0)+:\pm(0y\frac{1}{4})$ with $y\simeq1/10$. It was realized at this stage that the structure deduced for α′-cerium is of the α-uranium type (Jacob & Warren, 1937), in fact the first known example of this structure type other than uranium itself.

Our data do not permit a precise determination of the parameter *y*, and it will hence be assumed that it has the same value, $y=0{\cdot}105$, as found by Jacob & Warren for the α-U structure, but the accuracy is no better than $y=0{\cdot}105\pm0{\cdot}010$.

Calculated and observed intensities for α-U and α′-Ce are shown in Table 4. The calculated intensities are given as $I\propto|F/f|^2p$ 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.

Table 3. *Diffraction data for* α-Ce + α′-Ce

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

* 011 reflection from α″-Ce.

Table 4. *Intensities for* α-U *and* α′-Ce

		I_{obs}				I_{obs}	
HKL	I_{cal}	α-U	α′-Ce	*HKL*	I_{cal}	α-U	α′-Ce
020	0·2	*vw*	*vw*	202	8·0		*m*
110	5·0	*s*	*s*	221	15·0	*s*	
002	4·0	*s*	*m*	004	4·0		*vw*
021	7·5	*s*		042	6·1	*m*	
111	6·0	*s*	*s*	222	1·0	*vw*	*m*
022	0·5	*vw*	*t*	133	13·5	*m*	
112	10·0	*s*	*m*	024	0·5	*vw*	–
130	1·3	*vw*	–	114	10·0	*m*	*vw*
131	3·5	*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*
220	0·5	*vw*	–	152	15·6	*m*	

The bond lengths in α′-Ce at 58 kbar are Ce–2Ce $2{\cdot}90\pm0{\cdot}05$, Ce–2Ce $3{\cdot}05\pm0{\cdot}01$, Ce–4Ce $3{\cdot}36\pm0{\cdot}01$, Ce–4Ce $3{\cdot}49\pm0{\cdot}06$ Å. The bond angle for the two shortest bonds is $128\pm5°$, and endless zigzag 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.

4. The crystal structure of α″-Ce

The diffraction pattern of α″-Ce is quite similar to that of α-Ce, except that the f.c.c. diffraction lines have been split into components. This close relation is demonstrated in Table 5 which gives the data from a diffraction pattern taken at 41 kbar showing the presence of both α-Ce and α″-Ce, as well as 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 5. The cell dimensions deduced from the data of Table 5 are, 41 kbar pattern: α-Ce, $a=4{\cdot}629\pm0{\cdot}006$ Å, $V=24{\cdot}80$ Å^3; α″-Ce, $a=4{\cdot}806\pm0{\cdot}012$, $b=3{\cdot}194\pm0{\cdot}006$, $c=3{\cdot}196\pm0{\cdot}006$ Å, $\beta=92{\cdot}18\pm0{\cdot}40°$, $V=24{\cdot}51$ Å^3, $a:b:c=1{\cdot}508:1:1{\cdot}001$; 90 kbar pattern: α″-Ce, $a=4{\cdot}702\pm0{\cdot}010$, $b=3{\cdot}102\pm0{\cdot}005$, $c=3{\cdot}104\pm0{\cdot}005$ Å, $\beta=91{\cdot}99\pm0{\cdot}20°$, $V=22{\cdot}62$ Å^3, $a:b:c=1{\cdot}516:1:1{\cdot}001$.

Were β equal to 90° and the axial ratios $\sqrt{2}:1:1$ the monoclinic structure would become the f.c.c. structure.

Diffraction patterns of cerium metal taken at 56 and 100 kbar have been published by Schaufelberger & Merx (1974). A detailed analysis of their data shows that the bulk of their sample is α″-Ce. Table 6 gives the S values, obtained from their published 2θ values, for all lines due to the α″-phase (up to $S=1064$). It is seen that the agreement between observed and calculated S values is excellent. The unit-cell dimensions deduced from their patterns are, 56 kbar: $a=4{\cdot}762\pm0{\cdot}006$, $b=3{\cdot}170\pm0{\cdot}005$, $c=3{\cdot}169\pm0{\cdot}005$ Å, $\beta=91{\cdot}73\pm0{\cdot}15°$, $V=23{\cdot}91$ Å^3; 100 kbar: $a=4{\cdot}686\pm0{\cdot}006$, $b=3{\cdot}073\pm0{\cdot}005$, $c=3{\cdot}089\pm0{\cdot}005$ Å, $\beta=92{\cdot}69\pm0{\cdot}15°$, $V=22{\cdot}22$ Å^3.

Table 6. *Interpretation of the diffraction data reported by Schaufelberger & Merx* (1974)

	56 kbar			100 kbar		
HKL	S_{cal}	I_{obs}	S_{obs}	S_{cal}	I_{obs}	S_{obs}
$10\bar{1}$	177			182	–	
110	181	*vs*	181	192	*vs*	192
101	187			198	*vs*	198
200	223	*m*	222	231	*w*	231*
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		–
$12\bar{1}$	679			718	*s*	719
121	689	*s*	689	734		
112	695			738	*vs*	736
$20\bar{2}$	706		–	729		
220	726	*m*	727	767	*w*	764
202	747	*vw*	747	793	*w*	792
400	892	*w*	893	922	*vw*	922
022	1006	*w*	1005	1066	*m*	1064

* This diffraction line occurs at $2\theta=17{\cdot}49°$ according to the published patterns, but was omitted from the list of reflections given by Schaufelberger & Merx.

Table 7 is a list of diffraction lines reported by Schaufelberger & Merx which we have never observed and which remain unexplained.

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

Since the positions of the two atoms in the α″-Ce structure are (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, the calculated intensities are directly proportional to the multiplicity p. In Table 8 the values of p and the observed intensities are com-

Table 5. *Diffraction data for* α-Ce+α″-Ce *at* 41 kbar, *and for* α″-Ce *at* 90 kbar

α		α″		α+α″ 41 kbar		α″ 90 kbar		
HKL	S_{cal}	*HKL*	S_{cal}	*I*	S_{obs}	S_{cal}	*I*	S_{obs}
		$10\bar{1}$	172	*vw*	172	182	*vw*	180
111	177	110	179	*vs*	177	188	*vs*	188
		101	185			194		
		200	219	*m*	219	229	*w*	227
200	236			*w*	237			
		011	248	*m*	248	262	*vs*	262
		$21\bar{1}$	454	*w*	454	479	*w*–	479
220	471	211	479	*m*	474	505	*w*+	505
		020	495	*w*	495	525	*w*–	525
		002	495			525		
		$30\bar{1}$	598	*wD*	609	628	–	
		310	617			646	*w*	646
		301	635			664	–	
311	648			*wD*	647			
		$11\bar{2}$	661			701	*w*	703
		$12\bar{1}$	667			707		
		121	680	*wD*	680	719	*w*	721
		112	686			725		
		$20\bar{2}$	689			730	–	
222	707	220	714	*w*	711	754	*w*	755
		202	739			778		–

pared. As in α'-Ce there is evidence of preferred orientation.

Table 7. *Unobserved diffraction lines of Schaufelberger & Merx* (1974)

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

56 kbar pattern			100 kbar pattern		
Line No.	I_{obs}	S_{obs}	Line No.	I_{obs}	S_{obs}
4*	*w*	268			
5*	*w*	294	4*	*m*	308
			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

Table 8. α''-Ce *Intensities*

I is the 90 kbar pattern of Table 5, II the 56 kbar pattern of Table 6, III the 100 kbar pattern of Table 6 and IV the 65 kbar pattern of specimen 17709 with an unusual preferred orientation effect.

* Coincidence with α'-Ce lines.

		I_{obs}			
HKL	*p*	I	II	III	IV
$10\bar{1}$	2	*vw*			*s**
110	4	*vs*	*vs*	*vs*	*s**
101	2			*vs*	
200	2	*w*	*m*	*w*	*s**
011	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				
$30\bar{1}$	2	–	–	–	*w*+
310	4	*w*	*w*	*w*	*w*+
301	2	–	*w*	*w*	–
$11\bar{2}$	4	*w*	*s*	–	*vw*
$12\bar{1}$	4			*s*	
121	4	*w*	*s*	*vs*	*wD*
112	4				
$20\bar{2}$	2	–	–		
220	4	*w*	*m*	*w*	*vw*+
202	2	–	*vw*	*w*	–
400	2		*vw*	*vw*	*w*
022	4		*w*	*m*	*vw*

For five of our six samples, and the two patterns of Schaufelberger & Merx the intensity of a reflection *HKL* is enhanced relative to the companion reflection $HK\bar{L}$. This indicates a tendency of the plane $(10\bar{1})$ to align normal to the incident beam. However, in our sixth sample (17709) the $HK\bar{L}$ component is enhanced, indicating a tendency of the (101) plane to be oriented normal to the incident beam.

The bond lengths in the α''-Ce structure at 56 kbar are Ce–2Ce 3·169±0·005, Ce–2Ce 3·170±0·05, Ce–4Ce 3·235±0·010, Ce–4Ce 3·305±0·010 Å. Thus, as in α'-Ce there are four short and eight longer bonds. The short bonds form endless straight chains along the *b* and *c* axes.

5. Discussion

The results as to the variation of unit-cell dimensions of α'-Ce and α''-Ce with pressure are given in Table 9. It is seen that the two high-pressure phases have the same volume within experimental error. However, there is a small volume change (of about $\Delta V/V = 0{\cdot}011$) when the α-phase is transformed to the α' or α''-phase.

Nearly all 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 d 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 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 atmospheric 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 (about 0·1 Å) 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 observed variation of atomic volume with pressure for α-Ce is shown in Table 1 and Fig. 1. An 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. The results of this analysis are shown in Table 10. The same value $K = 1{\cdot}7 \times 10^{-3}$ kbar^{-1} is obtained for α-Ce in the range 40–51 kbar, for α'-Ce in the range 58–95 kbar and for α''-Ce in the range 56–100 kbar.

It is convenient to define the metallic radius for 12-coordination, R, in terms of the atomic volume per atom, V, by the equation (Zachariasen, 1973)

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

Pauling (1947) 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 $v = 3{\cdot}2$ for cerium in γ-Ce. The expected value for the metallic radius of cerium for $v = 3{\cdot}00$ is $R = 1{\cdot}851$ Å. 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 Å (Zachariasen, 1963). It is seen from Table 10 that the metallic radius of cerium of all three phases, α, α' and α'', extrapolated to atmospheric pressure from 50 kbar and above

Table 9. *Unit-cell dimensions for α′-Ce and α″-Ce*

Estimated error in the last decimal place is given in parentheses.

P (kbar)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	Second Phase	Phase V (Å^3)
α′-Ce							
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	tα″	–
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							
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	tα′	–
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 (6)	91·97 (30)	22·37	–	–
100	4·686 (6)	3·073 (5)	3·089 (5)	92·69 (15)	22·22	–	–

Table 10. *Various properties of the metal phases*

Phase	P (kbar)	K (10^{-3} kbar^{-1})	V (Å^3)	R (Å)	v
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
	7·5–25	4·1	28·52	1·714	3·77
	25–40	2·3	27·27	1·689	3·90
	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

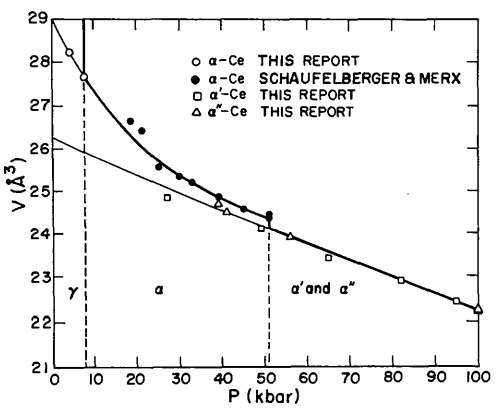

Fig. 1. The atomic volumes observed for α-Ce, α′-Ce and α″-Ce. The pressure – volume curve above 51 kbar (and its extrapolation to zero pressure) is based upon the two experimental points for α″-Ce at 56 and at 100 kbar, and an assumed constant compressibility. Only three experimental points above 51 kbar are given for α′-Ce, at 65, 82 and 95 kbar. The pressures were deduced from the unit-cell volumes observed for the coexistent α″-phase.

agrees with the predicted value for $v = 4{\cdot}00$. Indeed, the small value for the compressibility of $K = 1{\cdot}7 \times 10^{-3}$ kbar^{-1} observed for pressures above 50 kbar also indicates full tetravalency for cerium.

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