A NEW ALLOTROPIC FORM OF CERIUM DUE TO ITS TRANSITION UNDER PRESSURE TO THE TETRAVALENT STATE*

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An x-ray structural analysis on cerium under pressure was made in order to investigate its valence behavior in the metallic state. A new form, α'-Ce, always fcc but strongly collapsed, was found to exist at pressures higher than 50 kbar. It was deduced that Ce is tetravalent in the α' form. The atomic radius of Ce^{IV} was calculated, and the probable values of the valency in γ-Ce and α-Ce are also estimated.

Till now four allotropic forms of cerium have been known: a bcc δ phase, a dhcp β phase, a fcc γ phase, and a fcc α phase.[1] The first-order $\gamma \rightleftarrows \alpha$ transition, that occurs at 116°K and 1 atm or at 7670 atm and 298°K,[2] has been studied by several authors[3] and appeared due to a change in electronic configuration of cerium: Gschneidner and Smoluchowski,[4] from a critical review of the results, concluded that the most reliable values of the valence of cerium in the γ and α modifications are, respectively, 3.06 ± 0.06 and 3.67 ± 0.09. At the time they could not find any evidence to support the existence of a tetravalent state in metallic cerium. Recently Wittig,[5] investigating the electric properties of cerium under pressure, found at pressures higher than 50 kbar a new superconducting phase of cerium of unknown structure.

In order to extend the knowledge on the allotropy of cerium, a structural investigation has been carried out between about 7 and 100 kbar at room temperature by means of a high pressure x-ray camera (Model XKB-100), supplied by the Materials Research Corporation, using Mo $K_{\alpha\beta}$ radiation. The cerium used was a high-purity metal (99.95%) obtained by electrolysis. The calibration of the pressure was made using NaCl and Ag as markers and referring to their known compressibility data.[6,7] The accuracy in pressure measurements was ±1 kbar. The uncertainty in the lattice-parameter values was ±0.01 Å.

The experimental results, reported in Table I and Fig. 1, show that the α-Ce phase exists at room temperature between 7.6 and 50 kbar. In this pressure range the lattice constant decreases continuously, as pressure increases, from 4.85 to 4.73 Å.

At 50 kbar the fcc cell of α-Ce undergoes a drastic drop of 4.37% in volume: Its lattice constant varies discontinuously from 4.73 to 4.66 Å without any change in structure. The new fcc α'-Ce "collapsed" form appears to exist up to the highest pressure reached in this work (82.5 kbar) with a pressure-independent lattice parameter. All attempts to observe this phase in metastable conditions at pressures less than 50 kbar were unsuccessful with our exposure time of 12 h.

The first-order $\alpha \rightleftarrows \alpha'$ transition (like the γ

Table I. Experimental values of the lattice constant of cerium, at room temperature, as function of pressure, between 0 and 100 kbar.

Pressure[a] (kbar)	Lattice constant[b] (Å)	Pressure[a] (kbar)	Lattice constant[b] (Å)
Atmospheric pressure	5.16	54	4.66
10.5	4.82	56	4.66
11.5	4.83	62.5	4.66
14.5	4.81	63	4.66
15	4.82	67.5	4.66
21	4.79	70	4.65
26.5	4.78	71	4.66
36.5	4.75	72	4.66
46	4.73	74.5	4.66
49.5	4.73	78.5	4.66
49.5	4.66	82.5	4.66
53	4.67		

[a]All ±1 kbar.

[b]All ±0.01 Å.