

## X-RAY DIFFRACTION EVIDENCE FOR A CRITICAL END POINT FOR CERIUM I AND CERIUM II\*

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**Abstract**—A beryllium pressure vessel has been used to investigate the two face-centered phases of cerium at various temperatures and pressures along the phase boundary. X-ray diffraction records of the strong 111 peak of both phases show that the two peaks coalesce with increasing temperature and pressure along the boundary. The  $P$ - $t$  region for the critical end point of the boundary is obtained by extrapolation of the change in  $d$ -spacing with distance along the boundary, and is found to be 350–400°C and 20–22 kb.

The X-ray data also show that the compressibility and thermal expansion of the high-pressure (II) phase are greater than those of the low-pressure (I) phase.

Rate studies indicate that under pressure phase I persists into the phase II stability field with lowering temperature. Considerable overstepping of pressure into this field is also possible before complete transformation of I–II will take place.

### 1. INTRODUCTION

THE RARE earth element cerium (first of the lanthanum series) has been studied in great detail in the last 30 years with respect to atomic structure, magnetic susceptibility, alloy properties, and phase stability including polymorphism. HULL<sup>(1)</sup> and KLEMM and BOMMER,<sup>(2)</sup> recognized two polymorphs of cerium having identical densities, a close-packed hexagonal (h.c.p.) structure, and a face-centered (f.c.c.) cubic structure.

BRIDGMAN<sup>(3)</sup> at first found the compressibility of cerium to decrease in a normal way with pressure and found no transitions up to 12 kg/cm<sup>2</sup>. In a second series of experiments BRIDGMAN<sup>(4)</sup> located a transition in cerium at 7600 kg/cm<sup>2</sup> and 30°C, and also noted that the compressibility of the low-pressure-phase increased with increasing pressure, and decreased with increasing temperature. BRIDGMAN<sup>(5)</sup> again studied cerium of presumably high purity, this time finding no transition until he reached 12,430 kg/cm<sup>2</sup>, with the compression data,

however, in agreement with the results of 1927. In these and subsequent papers (BRIDGMAN<sup>(6–9)</sup>) these inconsistencies were explained to be the result of impurity differences, with the pure samples requiring higher pressures for transformation.

An anomalous behavior in thermal expansion was observed for the low-pressure phases of cerium by BARNSON, LEGVOLD and SPEDDING.<sup>(10)</sup> The expansion coefficient,  $\alpha$ , decreased with increasing temperature to a minimum at 200°C (where  $\alpha = 6 \times 10^{-3}/^\circ\text{C}$ ) and then increased regularly to 700°C. The minimum was suggested to be the result of formation of mixtures of both h.c.p. and f.c.c. phases.

The stability regions of the low- and high-pressure phases (hereafter called phases I and II, respectively) were determined using volume methods by LIKHTER, RYABININ and VERESCHAGIN.<sup>(11)</sup> Their results give a linear phase boundary with slope 23.8° C/kb and a transition pressure at 30°C of 8.7 kb.

From magnetic susceptibility measurements, TROMBE<sup>(12)</sup> and TROMBE and FOEX<sup>(13)</sup> noted a transformation with hysteresis and large volume change at low temperatures (100–200°K). More recent work with magnetic susceptibilities of

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erg cm<sup>-2</sup>)

$\lambda$	$\sigma$
065	19.701
050	19.039
143	43.168
119	41.731
175	52.793
219	53.411
206	62.116
216	62.057
181	20.339
146	19.801
397	44.568
348	43.301
486	54.504
625	54.871
572	64.130
624	64.048
145	21.339
114	20.816
318	46.759
273	45.515
388	57.186
497	57.628
457	67.284
493	67.294

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