

cerium by LOCKE⁽¹⁴⁾ and BATES and NEWMANN⁽¹⁵⁾ show further anomalies. Bates and Newmann also show that although the atomic radii of Ce and Th are 1.82 Å and 1.80 Å, respectively, there is a decrease in cell parameter (below 1.80 Å) when a small amount of Ce is present in Th; this slight decrease terminates and the cell parameter remains constant to about 35 per cent Ce in Th, after which the cell parameter increases with added Ce to the value for the pure metal.

To explain the above effect and also the temperature dependence of magnetic susceptibility of alloys in the Ce-Th system, Bates and Newmann suggest that the Ce ions resonate between the Ce³⁺ and Ce⁴⁺ state, thereby effectively producing a proportion of smaller ions with no 4f electrons. This concept is in keeping with the findings of WERNICK and GELLER⁽¹⁶⁾ who found that of all of the cobalt rare earth and nickel rare earth compounds having the Cu₅Ca structure only the cerium compounds depart from the plot of atomic volume vs. atomic number. The atomic volumes of Co₅Ce and Ni₅Ce are much too small for structures in which cerium is in the trivalent state. The promotion of the 4f electron into the 5d state, with corresponding contraction in ion size, is the explanation suggested by Wernick and Geller.

Evidence for a transition in cerium being due to electronic collapse has been found from neutron diffraction studies at low temperatures by WILKINSON, *et al.*,⁽¹⁷⁾ and from X-ray diffraction studies at low temperatures by SCHUCH and STURDIVANT⁽¹⁸⁾ and from high-pressure X-ray diffraction studies by LAWSON and TANG⁽¹⁹⁾ and ADAMS and DAVIS.⁽²⁰⁾ In all cases the high-pressure or low-temperature pattern conformed to a f.c.c. structure. Lawson and Tang obtained a cell constant of $a_0 = 4.84 \pm 0.03$ Å at room temperature and 15,000 atm. for the high-pressure phase ($a_0 = 5.14$ Å for the low-pressure phase at room temperature). The over-all volume change given by them is 16.5 per cent. Adams and Davis give $a_0 = 4.82_4$ at room temperature and transition pressure of 7 kb, with a volume change of 14 per cent at the transition and 18 per cent over-all.

PONIATOVSKII⁽²¹⁾ observed during a thermographic analysis of the two phases across the boundary that the heat of transition diminished to the point where it could not be separated from experimental error. This point was roughly 280°C

and 18.9 kb, thus indicating a critical end point for the phase boundary, although Pontiatovskii stated that the observed point where the heat of transition could not be detected was not necessarily the correct position for the end point.

Further volume work by HERMANN and SWENSON⁽²²⁾ and BEECROFT and SWENSON⁽²³⁾ confirms this result. The transition volumes decrease with increasing temperature and pressure along the boundary; Beecroft and Swenson extrapolate their data to 357°C and 20,000 atm as the point at which there is no volume change. Of importance in a later discussion will be the fact that Beecroft and Swenson observed a spreading out of the transition pressure at higher temperatures and a considerable increase in thermal expansion of cerium (presumably phase II) at 20,000 atm, over that of cerium at room pressure. The earlier work of HERMANN and SWENSON⁽²²⁾ revealed considerable hysteresis to the transition at room temperature, whereas the later work, using the cerium from the same source, revealed little or no hysteresis at room pressure.

2. EXPERIMENTAL METHOD

The apparatus is similar to that previously described by DAVIS and ADAMS.⁽²⁴⁾ A sketch of the supported beryllium pressure vessel is given in Fig. 1. The complete vessel with cap stands less than 6 cm high and is seated on a ram mounted at the base of a small press. The press, with attached spindle is inserted into the X-ray goniometer of a Norelco diffractometer as seen in the general experimental arrangement, Fig. 2.

The beryllium cylinder is encased in a steel jacket (C, Fig. 1) that is screwed into the hardened steel outer casing. In the present arrangement there is a selection of several bore sizes of Plug C and corresponding piston sizes (A and D) to allow for different sample sizes and pressure ranges for the pump system now in use. The sample and piston diameter used throughout the study was 4.6 mm. The sample pellet is separated from the piston face by a 4.6 mm × 1.25 mm. beryllium pellet to act as the window for the X-rays. The X-ray beam passes through slots in the outer casing (Fig. 1, inset), through the beryllium cylinder and pellet, and onto the sample. The "reflection" path is similar. The dial gauge arm operates a height indicator, the main function of which is to warn of excessive sample extrusion or deformation of the internal parts of the vessel.

Not shown in Fig. 1 is the heating jacket made from No. 24 (Brown and Sharpe) Nichrome V wire wound into a length of coil and fashioned into a zig-zag belt. The belt was insulated by an inner and outer layer of alundum cement baked at 500°C, or by layers of Transite and pure (99.9%) SiO₂ cloth held together by an