(Translated from Russian)

From: Journal of Physical Chemistry,
Vol. XXXI, No. 2, 1957, pp. 350-353.
Zhur. Fiz. Khim. 31, 350-3 (1957).

DETERMINATION OF THE HEAT OF TRANSITION IN CERIUM UNDER PRESSURE

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The phase transition in metallic cerium under high pressure, discovered by Bridgman (1), presents considerable theoretical interest. It has been previously established (2) that when this transition occurs there is a decrease in the constant a of the face-centered close-packed cubic lattice from 5.14 to 4.84 A corresponding to a 16.6% contraction in volume; there is no change in the type of crystalline lattice.

A basis exists for the assumption that the cerium transformation is due to a shift of a 4 f-electron to a 5 d state, i.e. to a transformation from a trivalent to a quadrivalent cerium. According to Zachariasen [see (2)] the ionic radii of trivalent and quadrivalent cerium with a coordination number of 12 should be 1.85 ± 0.01A and 1.71 ± 0.02A respectively, which is very close to values calculated on the basis of the observed lattice constants for "normal" and "close-packed" phases. The existence of the above-mentioned electron transition is confirmed also by data (3) on the accompanying sharp increase in the electrical conductivity of cerium.

Different values have been obtained in various studies for the pressure at which the cerium transition takes place. In 1927 Bridgman found a transition at 30° and 7600 kg/cm^2; at 75° the transition pressure was equal to 9400 kg/cm^2. Later (3) when working with cerium of unknown purity, he determined the transition pressure as being equal to 12,430 kg/cm^2. Finally, in 1951 (4) and 1952 (5), using extremely pure cerium, Bridgman observed a transition at a pressure of approximately 7000 kg/cm^2. The volume contraction at the transition has also not been accurately established. This is due to the fact that before the transition region is reached the compressibility of cerium increases rapidly with increase in pressure which makes it difficult to "delineate" the value of the volume contraction at the time of the transition itself. According to Bridgman (4) this value is approximately 8%; the over-all contraction in volume is 16.55% on changing pressure from atmospheric to 15,000 kg/cm^2.

This indeterminate volume contraction during transition impedes an accurate calculation of the latent heat of the studied transformation from the Clapyron - Clausius equation. However, the determination of this value is without any doubt of considerable interest. This paper is concerned with its experimental determination under high pressure.