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DETERMINATION OF THE HEAT OF THE PHASE TRANSFORMATION IN CERIUM  
UNDER PRESSURE

M. G. Gonikberg, G. P. Shakhovskoi,  
and V. P. Butuzov

Academy of Sciences of the USSR. Institute of Crystallography,  
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The phase transformation taking place ~~in cerium~~ in metallic cerium at high pressures, first discovered by Bridgman /1/, is of considerable ~~is~~ theoretical interest. It has now been established /2/ that in this transformation the constant  $a$  of the close-packed ~~f.c.c.~~<sup>fcc</sup> lattice falls from 5.14 to 4.84 Å, which corresponds to a 16.6% reduction in volume ; the type of crystal lattice undergoes no change.

There are grounds for believing that the cerium transformation in question is due to the passage of the 4f electron to the 5d level, i.e., to a transformation of cerium from the trivalent to the quadrivalent state. According to calculations of Zachariassen /2/, the ionic radii of ter- and ~~ter~~ quadrivalent cerium for coordination number 12 respectively equal.....and....., which are almost equal to the values calculated from the lattice



constants observed for the "ordinary" and "dense" phases. The assumption regarding the electron transition mentioned is also supported by  $\times$  data of /3/, relating to a sharp rise in the electrical conductivity of cerium after the transformation.

The pressure associated with the transformation in cerium has been estimated differently in different investigations. In 1927 Bridgman observed the transformation at  $30^\circ$  and  $7600 \text{ kg/cm}^2$ ; at  $75^\circ$  the transformation pressure was  $9400 \text{ kg/cm}^2$ . Later /3/, working with cerium of unknown purity, Bridgman found a transformation pressure of  $12,430 \text{ kg/cm}^2$ . Finally, in 1951 /4/ and 1952 /5/, using extremely pure cerium, Bridgman observed a transformation at a pressure of about  $7000 \text{ kg/cm}^2$ . The extent of the fall in volume during the transformation was also not established exactly. The reason for this was that, even before reaching the transformation region, the compressibility of cerium started rising rapidly with increasing pressure, which made it more difficult to "intercept" the extent of the change in volume associated with the transformation itself. According to Bridgman's estimate /4/, this quantity was about 8%; the total change in volume on raising the pressure from atmospheric to  $15,000 \text{ kg/cm}^2$  was 16.55%.

The indeterminacy in the extent of the fall in volume attributable to the transformation made it difficult to carry out an exact calculation of the latent heat of the transformation from the Clausius-Clapeyron equation. A determination of this quantity is nevertheless of very great interest. In this paper we shall consider its determination under high-pressure conditions.



### Experimental Part

In order to determine the heat of the phase transformation of cerium under pressure we used the thermogram method (see /6/). The use of the thermal-analysis method at high pressures is described in /7, 8/. The essence of the method employed lies in comparing the areas of the differential records of the thermogram of ~~the substance under examination with that~~ of another standard substance for which the thermal effect of the phase transformation is known. Usually the standard is a substance in which a phase transformation takes place at a temperature fairly close (but not equal) to that of the phase transformation in the substance under consideration. Under these conditions (for a constant heating rate), the areas of the ~~the~~ differential records of the thermograms are proportional to the heats of the transformations and to the amounts of the substances taken. In our method the work was carried out at constant temperature but increasing pressure ; hence our standard had to be a substance in which the phase transformation took place at a pressure not equal to but close to that of the cerium transformation. Mercury provided such a standard. The melting curve of mercury is quite well known /9, 10/. In Bridgman's paper /9/ this curve <sup>was used</sup> (together with data relating to the compressibility of solid and liquid mercury) ~~were used~~ to calculate its heat of fusion at pressures up to 12,000 kg/cm<sup>2</sup> (corresponding to a melting point of 22.2°).

We used cerium of 97% purity.\* As will be shown later, the

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\* Containing 1.5% Nd, 1.3% Pr, 0.1% Pb, and 0.01% Sn.



the phase transformation of this cerium took place at pressures close to those found for pure cerium by Bridgman in his latest papers /4, 5/. In calculating the heat of the transformation a correction was made for the 3% of "inert" impurities.

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Fig. 1. Schematic section of the high-pressure vessel. 1) electrical conductor ; 2) resistance manometer ; 3) cylinder containing the cerium ; 4) body of the vessel ; 5) copper block ; 6) cylinder containing the mercury ; 7) thermocouple ; 8) ebonite bushing.

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The experiments were carried out in a high-pressure booster with a working channel 25 mm ~~long~~ across, this being sufficient to create the required hydraulic (pentane) or gas (nitrogen) pressure. A copper block 5 was mounted on the electrical conductor ~~at~~ 1 (Fig. 1). The cerium and mercury samples 3 and 6 under consideration were placed in two similar small cylinders made of plexiglass (wall thickness 1.5 mm and internal diameter 6 mm), firmly fixed in the block 5. The rise in temperature associated with the phase transformations (solidification of mercury or transformation of cerium into the denser form) was measured with a differential thermocouple 7 made of iron and Nichrome, coated with a thin layer of shellac, and recorded with a Kurnakov pyrometer. The "hot" junctions of the thermocouples were centered in the cylinders by means of the ebonite bushings 8.

The rate of pressure rise was the same in all the experiments.



The rise in pressure from 4000 to 13,000 kg/cm<sup>2</sup> (in experiments with hydraulic pressure created by pentane) was achieved in 11 min. The pressure was measured by a Manganin resistance manometer 2 to an accuracy of  $\pm 30$  kg/cm<sup>2</sup>. The rate of pressure rise increased slightly during compression owing to the fall in the compressibility of the medium transmitting the pressure. This could cause error in measuring the thermal effects owing to the change in the conditions of heat transfer. In order to find the extent of this possible error we made some experiments on the solidification of mercury under gas pressure (Nitrogen) as well as pentane. The ~~area~~ area of the differential records of the thermograms for the same weight of mercury was almost the same in the two cases (discrepancy 3%). Subsequent experiments were made with the booster channel filled with pentane.

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Fig. 2. Typical thermogram taken with increasing pressure and constant temperature.

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In order to check the accuracy of the method we also made 15 experiments in which the same amount of mercury was poured into each of the cylinders and the rise in temperature on solidification was measured with two differential thermocouples connected to two mirror galvanometers with photorecording on the same drum. Each thermocouple was connected now to one and now to the other galvanometer. On the basis of these experiments we estimated the maximum possible error in determining the thermal effect of



the phase transformation as  $\pm 5\%$ .

In order to determine the heat of the phase transformation in cerium the latter was first melted in vacuum in a quartz tube and then machined to fit the cylindrical container exactly. The thermocouple was fixed tightly in a hole drilled in the center of the sample. The experiments were made with one differential thermocouple, the junctions of which were placed in the mercury and cerium samples. The weight of mercury was 2.00 g in all the ~~xxx~~ experiments and that of the cerium 1.15 g.

A typical thermogram is illustrated in Fig. 2. The first jump in temperature (on the left) corresponds to the phase transformation of cerium and the second (on the right) to the solidification of mercury.

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Table 1

Results of Determining the Heat of the Phase Transformation in Cerium

Key

- 1) ~~Series~~ No. of the series
  - 2) Pressure at the onset of the phase transformation,  $\text{kg/cm}^2$
  - 3) Areas of the differential records of the thermograms,  $\text{mm}^2$
  - 4) Heat of phase transformation of cerium, cal/g-atom
  - 5) Average
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The results of three series of experiments are shown in ~~the~~ Table 1. In the last column of the table we give the heat

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of the phase transformation in cerium  $Q_{Cd}$  calculated from the formula \*

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where  $q_{Hg}$  is the heat of fusion of 1 g of mercury according to Bridgman's data /9/ at the temperature of the experiment, <sup>and</sup>  $K$  is the ratio of the areas of the differential record of the thermograms ( $S_{Ce} : S_{Hg}$ ).

The average value of  $Q_{Ce}$  from the three series of experiments (a new pair of samples and new thermocouples were taken for each series) equals  $880 \pm 40$  cal/g-atom.

#### Discussion of Results

The results of the present investigation confirm the identity of the ~~form~~ <sup>type</sup> of cerium formed at high pressures with the low-temperature form. Earlier Trombe and Foex /11/ ~~xx~~ studied the behavior of cerium at low temperatures and observed <sup>a</sup> ~~its~~ transformation at  $109^{\circ}K$ , with a 10% fall in volume. In connection with this it was first suggested in /2/ that the form of cerium found by Trombe and Foex was identical with that discovered by Bridgman /1/ at high pressure. Two papers were later published in support of this view. Shuch and Sturdivant /12/ reported their earlier x-ray diffraction study of the crystal structure of cerium at  $90^{\circ}K$ .

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\* We consider the cerium transformation as completed since the pressure in our experiments went up to  $13,000 \text{ kg/cm}^2$ ; at this pressure the less dense form could not be detected by x-ray diffraction. (see /2/).



In this they observed the existence of two crystalline phases, one with the ordinary fcc lattice ( $a = 5.12 \text{ \AA}$ ) and the other with a compressed lattice of the same type ( $a = 4.82 \text{ \AA}$ ), i.e., with the same parameters as in /2/.

Measurements of the electrical resistance of cerium at low temperatures /13/ indicate that the new, denser form of cerium has a considerably lower resistance than the one existing at ordinary temperatures.

Lawson and Ting-Yan-Tang /2/ not only suggested the identity of the two forms of cerium in question but also made an approximate estimate of the heat of the transformation under pressure so as to be able to plot the p-T diagram satisfying this concept. According to these calculations, the heat of the cerium transformation should in this case be about  $0.04 \text{ eV}$ , or about  $900 \text{ cal/g-atom}$ . Our ~~The~~ experimental ~~is~~ value of  $880_{\pm 40} \text{ cal/g-atom}$  (at  $13$  to  $18^{\circ}\text{C}$ ) is extremely close to this value. It should be mentioned that the plotting of the p-T curve directly from experimental data relating to the temperature of the phase transformation as a function of pressure is complicated in the case of ~~the~~ cerium by kinetic factors (the retardation and incompleteness of the transformation at low temperatures), as indicated in /11/.

### Conclusions

1. We have described the ~~use~~<sup>application</sup> of the thermographic method to the case of high pressures, the principle being to compare the thermal effects of the phase transformations of the substance under con-



sideration with that of a standard substance at neighbouring but different ~~temperatures~~<sup>pressures</sup> and constant temperature.

2. We have determined the heat of the phase transformation of cerium, which is equal to  $880 \pm 40$  cal/g-atom at temperatures of 13 to  $18^{\circ}\text{C}$  and a pressure of about  $7000 \text{ kg/cm}^2$ .

3. Our results support the view that the form of cerium observed at high pressures is identical with that observed at low temperatures.

#### LITERATURE CITED

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