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UNDER PRESSURE

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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 Å 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 ± 0.01 Å and 1.71 ± 0.02 Å 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/cm²; at 75° the transition pressure was equal to 9400 kg/cm². Later (3) when working with cerium of unknown purity, he determined the transition pressure as being equal to 12,430 kg/cm². Finally, in 1951 (4) and 1952 (5), using extremely pure cerium, Bridgman observed a transition at a pressure of approximately 7000 kg/cm². 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/cm².

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.

Experimental Method

In order to determine the heat of transition in cerium under pressure we used the thermogram [see (6)] method. The application of the thermal analysis method at high pressures is described in paper (7,8). The method consists in comparing the areas of differential thermogram recordings for a substance with a known phase transition heat and for the substance studied. Usually the substance chosen for a standard is one in which the phase transformation takes place at a temperature not equal to but near that of the transformation temperature of the substance being studied. Under these conditions (with a constant rate of heating) the areas of the differential thermogram recordings are proportional to the transformation heats and the quantities of the substances used. According to our method we carried out the experiment at constant temperature, but under increased pressure; therefore, we had to choose for our standard a substance whose phase transition took place under a pressure not equal to but near that of the transition pressure in cerium. We used mercury as a standard. The curve for mercury fusion has been sufficiently studied [see for example (9,10)]. Using such a curve and using data for the compressibility of solid and liquid mercury Bridgman (9) calculated the heat of fusion of mercury at pressures up to $12,000 \text{ kg/cm}^2$ (which corresponds to a melting point of $22,2^\circ$).

We used 97% pure cerium.* As will be shown the phase transformation of this cerium took place under pressures close to those found for pure cerium by Bridgman in his most recent papers (4,5). A 3% correction for "inert" admixtures was made in calculating the transition heat.

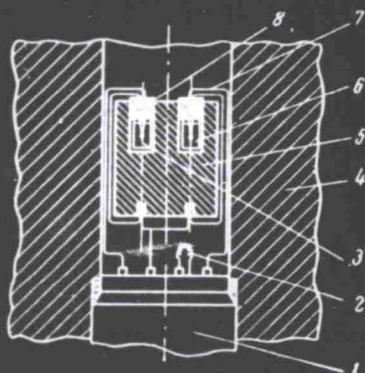


Fig. 1. Schematic cross section of high pressure container. 1 - electric lead; 2 - resistance manometer; 3 - cup with cerium; 4 - body of container; 5 - copper block; 6 - cup with mercury; 7 - thermocouple; 8 - ebony bushing.

The experiments were carried out in a high pressure intensifier having a working canal diameter of 25 mm permitting the formation of the necessary hydraulic (pentane) and gaseous (nitrogen) pressure. A copper block 5 was attached to the electric lead 1 (Figure 1). Samples of cerium 3 and mercury 6 were placed in two identical plexiglass cups (having 1.5 mm thick walls and an interior diameter of 6 mm) mounted securely in the block 5. The increase of temperature during phase transitions (solidification of the mercury, transition of cerium into a more compact modification) was measured by means of a differential iron-Nichrome thermocouple 7, covered with a thin layer of shellac and recorded by a N.S. Kurnakov pyrometer. The "hot" junctions of the thermocouples were centered in the cups by means of ebony bushings 8.

* It contained 1.5 per cent neodymium, 1.3 per cent praseodymium, 0.1 per cent lead and 0.01 per cent tin.

The rate of increase of pressure was the same in all experiments. The increase in pressure from 4000 to 13,000 kg/cm² (in experiments where the hydraulic pressure was generated by pentane) was reached within 11 minutes. The pressure was measured by a manganin resistance manometer 2, accurate within ± 30 kg/cm². The rate of increase in pressure increased somewhat during compression as a result of a decrease in the compressibility of the medium which transmitted the pressure. This could account for error in the measurements of heat effects due to changes in the heat transfer conditions. In order to determine the magnitude of such a possible error we carried out experiments on the solidification of mercury under gas pressure (nitrogen) and pentane. The differential area between the thermogram recordings for identical weighed portions of mercury in these experiments was practically the same (3% divergence). Further experiments were carried out with the intensifier canal filled with pentane.

In order to determine the accuracy of this method we also carried out 15 experiments in which both cups held an equal amount of mercury; the increase in temperature on solidification was measured by means of two differential thermocouples attached to two mirror galvanometers photo-recording one drum. Each thermocouple was attached first to one then to the other galvanometer. On the basis of these experiments we have calculated at $\pm 5\%$ the maximum possible error in the phase transition heat.

In order to determine the phase transition heat in cerium the latter was prefused in a vacuum in a quartz tube and was then turned down to the exact dimensions of the cup. The thermocouple was securely placed in the opening which was drilled in the center of the sample. The experiments were carried out with one differential thermocouple, the junctions of which were placed in the mercury and cerium samples. The weighed portion of the mercury in all of the experiments was equal to 2.00 g and of the cerium to 1.15 g.

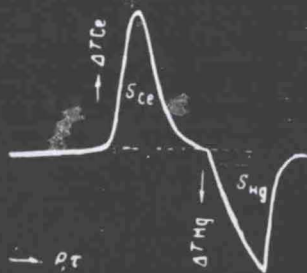


Fig. 2. Typical thermogram taken at constant temperature and increasing pressure.

A typical thermogram is shown in Figure 2. The first temperature discontinuity (on the left) corresponds to the cerium phase transition; the second (to the right) corresponds to the solidification of mercury.

The results of three experimental series are shown in the table.

In the last column are given the values of the heat of transition for cerium calculated according to the

| No. of cerium | T, °C | Pressure at beginning of phase transition, kg/cm ² | | Areas of differential thermogram recording, mm ² | | Ce S _{Hg} | Heat of transition in cerium cal/g atom |
|---------------|-------|---|-------|---|------|-----------------------|---|
| | | Ce | Hg | Ce | Hg | | |
| 1 | 13,2 | 6700 | 10400 | 3470 | 3140 | 1,11 | 880 |
| | | 6850 | 10350 | 3470 | 3130 | 1,11 | |
| | | 6850 | 10350 | 3440 | 3150 | 1,09 | |
| | | 6700 | 10350 | 3410 | 3050 | 1,12 | |
| | | | | 3480 | 3140 | 1,11 | |
| | | | | Average | 1,11 | | |
| 2 | 17,0 | 7000 | 11300 | 3110 | 2960 | 1,05 | 840 |
| | | 6850 | 11000 | 3150 | 3010 | 1,04 | |
| | | 6900 | 10900 | 3190 | 2960 | 1,08 | |
| | | | | 3150 | 2950 | 1,07 | |
| | | | | | | Average | |
| 3 | 18,2 | 7200 | 11200 | 3630 | 3140 | 1,16 | 920 |
| | | 7100 | 11300 | 3780 | 3160 | 1,19 | |
| | | 7150 | 11200 | 3850 | 3100 | 1,15 | |
| | | 7100 | 11300 | 3600 | 3130 | 1,15 | |
| | | | | | | Average | |

formula

$$Q_{Ce} = \frac{2.00 \cdot 140.13}{1.15 \cdot 0.97} q_{Hg} \cdot K$$

where q_{Hg} is the heat of fusion of 1 g mercury at the temperature of the experiment according to Bridgman (9); K is the ratio of the differential thermogram recording (S cerium: S mercury).

The average value Q_{Ce} from the three experimental series (new weighed portions of the samples and new thermocouples were used for each series) is equal to 880 ± 40 cal/g atom.

Discussion of the Results

The results of the present investigation confirm the opinion concerning the identity of the cerium modification which takes place under high pressures with its low temperature modification. Previously Trombe and Foex (11) studying cerium behavior at low temperatures found its transformation at 109° K with 10% contraction in volume. In this connection the supposition was first made in paper (2) that the cerium modification found

*We consider the cerium transformation completed as the pressure in our experiments rose to 13,000 kg/cm²; at such a pressure a less compact modification is not revealed by means of x-rays [see (2)].

by Trombe and Foex is identical to that discovered by Bridgman (1) under high pressure. Two papers were published later confirming these suppositions. Schuch and Sturdivant (12) described their previously carried out x-ray study of the crystalline structure of cerium at 90°K. They had then found the presence of two crystalline phases: with a normal face-centered cubic lattice ($a = 5.12\text{\AA}$) and with a close-packed lattice of the same type ($a = 4.82\text{\AA}$), that is with the same parameters as in paper (2).

Results of studies of the electrical resistivity of cerium at low temperatures (13) confirms that fact that the new more compact modification of cerium has a considerably lower resistivity than the modification which exists at normal temperature.

Lawson and Ting-Yan-Tang (2) expressed not only the supposition that the two mentioned modifications of cerium are identical but also carried out an approximate evaluation of the magnitude of the transition heat under pressure which would allow the construction of a p-T diagram satisfying this condition. According to their calculations the transformation heat of cerium must in this case be close to 0.04 ev, i.e. close to 900 cal/g atom. The experimental value of 880 ± 40 cal/g atom which we found (at 13 - 18°C) is very close to this value. It must be noted that the construction of the p-T curve directly from experimental data on the phase transition temperature as a function of pressure in the case of cerium is complicated by kinetic factors (friction and incomplete transition at low temperatures) [see (11)].

Conclusions

1. The application of the thermogram method for high pressures has been described; it is based on a comparison between the heat effects of the phase transformation of the substance studied and a standard at different (but close) pressures and constant temperature.
2. The heat of transition of cerium has been determined as equal to 880 ± 40 cal/g atom at temperatures of 13 - 18°C and a pressure of about 7000 kg/cm².
3. The results of the study confirm the identity of the cerium modification which takes place under high pressure with its low temperature modification.

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