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THE PHASE DIAGRAM FOR CERIUM

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The p–T diagram of 99.8% pure cerium has been measured from – 150° to + 100°C over a pressure interval up to 12,000 kg/cm^2. In the p–T plane the phase equilibrium line is a straight line whose slope is 43 kg/cm^2–°C. It is shown that the transition at atmospheric pressure and low temperature is the same as that which occurs at room temperature and high pressure.

BRIDGMAN has observed a polymorphous transition in cerium at high pressure. His data on the transition pressure, however, is inconsistent. In 1927 he found[1] that the transition pressure was 7600 kg/cm^2 at 30°C and 9400 kg/cm^2 at 75°C. Later data[2] gave 12,430 kg/cm^2 at room temperature, which Bridgman explained in terms of the insufficient purity of his old sample. Later measurements of the electric resistance[3] showed, however, that the transition lies in the vicinity of 7000 kg/cm^2 at room temperature.

Lawson[4] has used x-ray methods to investigate the structure of cerium above the transition pressure, and found that on passing through the transition the lattice remains face-centered cubic. All that happens is that the lattice constant decreases by amount corresponding to the sum of the volume change in the transition and the compressibility of cerium. In addition, it is known that at atmospheric pressure cerium undergoes a transition with a volume change of the order of 10%; when the temperature is lowered, this transition takes place at – 164°C, and when it is raised, the transition occurs at – 98°C. All the data with respect to this transition has been collated by Trombe and Foëx.[5] X-ray investigations[6] have shown that the lattice again remains face-centered cubic and that only the lattice constant changes.

It is known that at room temperature cerium has two modifications, the face-centered cubic and the close-packed hexagonal. This latter modification is obtained by slow cooling from 400°C, and for it no low-temperature polymorphous transition is observed. Up to the present, however, the question of the relation between the low-temperature and the high-pressure transitions has remained unanswered. In order to clarify this subject we have measured the temperature dependence of the cerium transition pressure in the temperature range from – 185 to + 100°C on an instrument designed for measuring compressibility of solids.

This instrument (Fig. 1) is a multiplier whose low-pressure press has a piston 1 without packing, so that friction losses are reduced to a minimum. This piston is carefully ground to fit a cylinder 2 with a clearance of about 0.05 mm for a diameter of 192 mm. This high piston diameter makes it possible to operate at relatively low oil pressures in the cylinder (of the order of tenths of a kg/cm^2), so that with a highly viscous oil (in our case, castor oil) there is little leakage through the clearance. The leakage losses are compensated for by a fine regulation valve leading to a reservoir in which the oil pressure is maintained by an air cushion. In this way one may maintain a given constant pressure on the cylinder, or

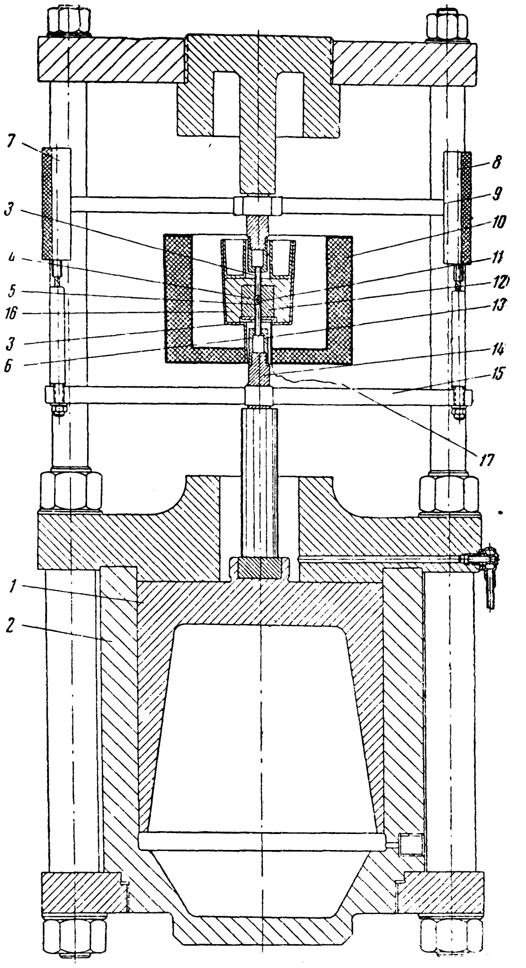

FIG. 1. Schematic diagram of the apparatus.

increase it smoothly to a given value. The high pressure is applied within a "pobedit"* piezometer 12 to the sample 4 which is surrounded by a lead casing 11; the low shear strength of lead makes it possible to apply a hydrostatic pressure distribution to the sample. For toughness the piezometer is conical with a vertex angle of 0.5° and pressed into a die 16 made of 45 KhMFA steel heat treated to a Rockwell hardness of 49. The inner opening of the piezometer has a diameter of 6 mm and is carefully ground by means of diamond powder. Two pobedit pistons 3, the upper and lower plunger, enter into it. The clearance between these pistons and the piezometer is no greater than 0.02 mm along the diameter. This small clearance is possible because Young's modulus of pobedit is three times greater than that of steel, and even at a pressure of 30,000 kg/cm^2 the lateral deformation of the pobedit pistons is less than 0.01 mm, so that the rods cannot be pressed against the walls of the piezometer. The rods were sectional, so that complicated pobedit parts could be avoided. Into the bearing 13 made of soft steel are pressed a pobedit plunger 3 of diameter 6 mm, a short rod 6 of diameter 9 mm, and a steel supporting part 14. The short rod 6 is necessary to keep 3 from cutting into the steel. Measuring levers 160 mm long are attached to 14. Attached to the lower level 15 are supports, and to the upper one 9 are dial indicators 7 and 8 with divisions indicating in microns. Two indicators are necessary to eliminate possible effects due to bending, and the actual displacement of the rods in the piezometer is determined from the average of the readings. The more accurately centered the plungers are in the press, the less is the difference in the indicator readings.

In order that the lead not flow through the clearance gap between the piezometer and rods, conical steel sealing rings 5 are placed on their ends. The piezometer is surrounded by a brass container 10 into which one may place a cooling mixture or boiling water. The container is wrapped with "mipor" thermal insulation. The temperature is measured outside the pobedit piezometer by a copper-constantan thermocouple. In view of the high mass of the piezometer, one may assume that the temperature in its interior, or that of the sample, hardly differs from the temperature measured by the thermocouple 17. A temperature difference even of 5°C would hardly alter the accuracy of the results, since the uncertainty in the pressure is ± 300 kg/cm^2 and the slope of the line in the phase diagram (see Fig. 3) is about 43 kg/cm^2-°C.

A sample of height 5 mm and diameter 5 mm is pressed into a lead casing and placed between the rods in the piezometer. After preliminary compression to the maximum pressure, the cylinder pressure is slowly raised. The oil pressure is obtained from a standard manometer. When the manometer reading is integral, readings are taken on both displacement indicators.

When the maximum pressure is reached, the control valve is cracked so that the cylinder oil pressure drops at approximately the same rate as that at which it was raised. There then results a "hysteresis" loop in the rod displacement-pressure diagram; the two branches of this loop correspond to increasing and decreasing pressures. The difference between these two curves is explained by friction, which is the total of friction in the low-pressure cylinder and friction in the piezometer as the rods move in it. When the pressure is being raised, additional effort must be expended to overcome friction, and when the pressure is being lowered the friction force is subtracted. Therefore the distance between the two branches of the loop for a given value of the displacement corresponds to twice the friction, and in order to elimi-

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* "Pobedit" is a solid powder alloy developed in the U.S.S.R. composed of tungsten carbide powder combined with cobalt under heat and pressure—Tr.

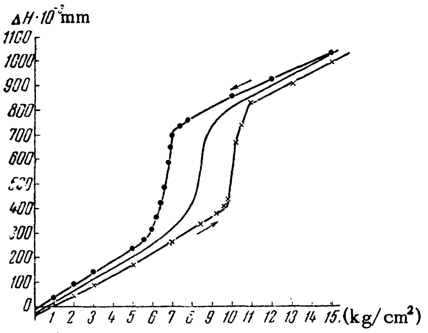

FIG. 2. The displacement H of the piezometer rods as a function of the pressure in the cylinder of the press, for increasing and decreasing pressure.

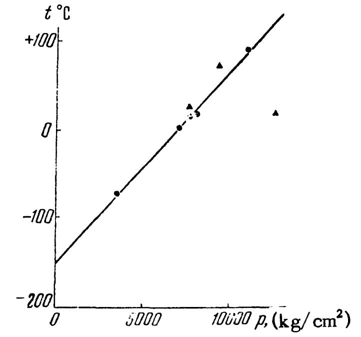

FIG. 3. Phase diagram of cerium. The pressure dependence of the polymorphous transtion temperature between phases I and II; ● — our data, ▲ — Bridgman's data.

inate this effect one need only draw an average line through this loop, thus obtaining the actual pressure dependence of the rod displacement. Now from this curve one can subtract the compressibility of the sample being investigated. If a polymorphous transition takes place in the sample, the start of this transition is observed by the rapid rate at which the readings change. When this occurs, the pressure is held constant or increased very slowly, in order that the whole transition take place in the smallest possible pressure interval. Figure 2 shows a characteristic hysteresis loop for cerium at 17° C. The beginning of the transition is very clearly seen, and a large part of the transition takes place in a sufficiently narrow pressure interval, but the end of the transition is somewhat spread out. The same pattern is observed as the pressure is decreased. The transition pressure as given by the average line, and the average of the transition pressures obtained by finding the beginning of the transition for increasing and decreasing pressures differ by a value less than the limits of experimental accuracy, which we take as ±300 kg/cm^2.

Figure 3 shows the p–T diagram obtained for cerium; it can be represented with sufficient accuracy by a straight line. The points obtained by Bridgman in 1927 (see above) lie in the vicinity of this line. The lowest point in Fig. 3 corresponds to the measurement at −71°C, for which the whole hysteresis loop was obtained. At −185°C, the transition started at 1000 kg/cm^2, but the opposite transition was not observed when the pressure was decreasing. The point at which the transition starts at −185°C lies on the same line as similar points for higher temperatures. It is therefore valid to extrapolate the p–T line to the temperature axis. The intersection is at T = −150°C, which corresponds to the transition observed in cerium at low temperatures and atmospheric pressure. The results of measurement are shown in the table.

The cerium was obtained from the Institute of Rare Metals, and contained 99.8% Ce.

From the rod-displacement-pressure curves obtained for each temperature, we can evaluate the volume change in the transition. An exact determination of this quantity is made difficult by the fact that the beginning and end of the transition are not very sharply indicated on the average line. We have therefore obtained only the average value Δv ≈ 8% (Bridgman obtained 7.68%). We note that as the temperature increases, Δv clearly decreases. If the p–T diagram is known, the Clausius-Clapeyron equation can be used to find the heat of transition; we obtain 0.023 ev at 20°C. The question of why Bridgman obtained 12,430 kg/cm^2 for the transition pressure remains unanswered. One may suggest that this deviation can be explained by the different thermal histories of the samples and by different concentrations of the cubic and hexagonal phases. An answer to this question requires continuation of our investigations with cerium.

Points of the cerium p-T diagram

T (°C)	p (kg/cm²)
+94.5	11100
+20	8100
+17	7600
+ 4	7150
—71	3550
—150 (extrap.)	1

We consider it our duty to express our gratitude to I. V. Brandt for aid in the work.

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