PHASE DIAGRAM OF CERIUM IN THE RANGE 20—350°C *UP TO PRESSURES OF* 80×10^3 kg/cm²

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The phase diagram of the transition $\gamma \rightleftarrows \alpha$ in cerium was extended to 350°C. It was found that near 200°C the boundary between the regions of existence of the γ- and α-phases deviates from linearity toward the temperature axis. It was established that at the transition the relative change of resistance $\Delta R/R_\gamma$ remains finite up to 350°C and decreases nonlinearly with rising temperature beginning at 170—180°C; this does not allow extrapolation of the resistance change to zero temperature. Thus the results obtained fail to confirm the existence of a critical point up to 350°C and the possibility of the existence of this point is doubtful in the light of these results. The existence of a minimum and a maximum in the dependence R(p) was confirmed for cerium at pressures slightly larger than 50×10^3 and 70×10^3 kg/cm² respectively. It was also found that temperature rise increases the pressures at which these extremal points occur.

THE isomorphic transformation $\gamma \rightleftarrows \alpha$ in cerium (fcc structure) has recently been closely studied in quite a wide range of pressures and, especially, of temperatures. The latest data on this transformation are given in the work of Itskevich.[1]

One of the results of the recent studies was the advancement of the suggestion that near 300°C at 20×10^3 kg/cm² the boundary separating the regions of existence of the α- and γ-phases vanishes at a critical point above which there is no discontinuous change in the properties of the metal characteristic of a first-order transition. This suggestion has not yet been proved by direct experiments but the following features of this polymorphic transition are cited in its support: 1) both modifications of cerium have the same lattice;[2] 2) the jumps in the macroparameters (ΔV, ΔQ) of the transition $\alpha \rightleftarrows \gamma$ decrease with increase of the transition temperature;[3,4] 3) near the transition the high-temperature γ-phase has anomalously high compressibility which is much greater than the compressibility of the α-phase. The temperature coefficients of the resistance of the two phases are such that extrapolation indicates the equality of the resistivities of the two phases at 300°C.[1]

Linear extrapolation of the macroparameter discontinuities to zero and estimates of the coordinates of the critical point were based on the linearity of the boundary separating the α- and γ-phases in the (p, T) plane, i.e., on the constancy of the left-hand part of the Clapeyron-Clausius equation.

Less known are the properties of cerium at pressures above 30×10^3 kg/cm². However, it is known from the pressure dependence of the electrical resistance of cerium at room temperature[5,6] that the resistance of the α-phase decreases with increase of pressure up to about 50×10^3 kg/cm², then it passes through a minimum and rises by about 10% in the region of 70×10^3 kg/cm². On further increase of pressure the resistance continues to decrease. This form of the dependence R(p) of cerium gives grounds for assuming that in the quoted range of pressures there is a second polymorphic transition.[5] This transition, if it exists, is undoubtedly of great interest because it represents further compression of the compressed fcc (fcc'[1]) lattice.

The purpose of the present work was to carry out a direct experimental study of the transition $\gamma \rightleftarrows \alpha$ in the region of the supposed "critical" temperatures and pressures, and to find more accurately the behavior of the electrical resistance of cerium at pressures above 30×10^3 kg/cm² and high temperatures.

EXPERIMENTAL TECHNIQUE AND SAMPLES

Apparatus with a piston piezometer, described in earlier work,[7] was used to measure pressures up to 30×10^3 kg/cm². The phase transition was

detected by the discontinuity in the electrical resistance. For this purpose a sample in the form of a narrow strip (0.5 × 0.5 mm in cross section) and having an initial resistance R_0 = 0.1—0.4 Ω (varying with length) was placed in a pellet of cesium chloride and located on the axis of the channel in a high-pressure vessel (piezometer) between the moving and fixed plungers. The fixed plunger was insulated with mica from the piezometer casing. The piezometer was heated in a tubular furnace to a temperature not exceeding 350°C with the plungers lightly loaded in a press. When the required temperature was established the force applied to the moving plunger (and consequently the pressure in the piezometer) was raised gradually and then lowered. Readings of the voltage drop across the sample for a fixed current were taken at equal intervals of the applied mechanical force F. Owing to friction, the R(F) curves for rising and falling pressures did not coincide but formed hysteresis loops which are usual in this technique.

The phase transition was represented by the discontinuities on the rising and falling branches of the hysteresis loop obtained in this way. The magnitude of the electrical resistance discontinuity ΔR at the phase transition was determined directly from the graph by extrapolation of the branches corresponding to α- and γ-phases to the beginning of the transition for increasing and decreasing pressures as shown by the dashed lines in Fig. 1. The transition pressure was taken to be the average of the pressures at the beginning of the transformations $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$. Measurements

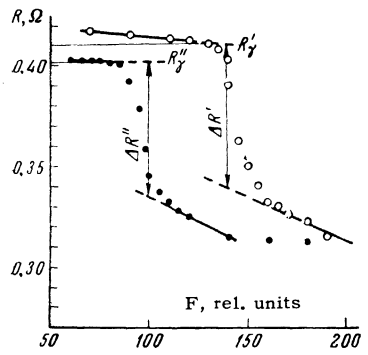

FIG. 1. Experimental curve of the dependence of the electrical resistance of cerium No. 1 on the press load at 135°C: o – increasing pressure, • – decreasing pressure. The dashed lines show extrapolation of the branches of R(F) for the γ- and α-phases. ΔR′ and ΔR″ are, respectively, the electrical resistance discontinuities at the transitions $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$; R'_γ and R''_γ are the resistances of the sample in the γ-phase, reduced to the extrapolated starting points of the transitions for rising and falling pressures respectively.

were carried out on samples of cerium with the lowest impurity content among those available to the authors. The same material has been used earlier [7] and was called cerium No. 1.

In contrast to measurements at pressures up to 30 × 10^3 kg/cm^2 the dependences R(p, T) for cerium at higher pressures were found by heating the samples directly by the measuring current (different apparatus was used). The resistance was calculated from the voltage drop across the sample at the known value of the current. The sample temperature was estimated from the electrical power supplied to it. The metal samples and the medium transmitting pressure were the same as in the piston piezometer measurements. To reduce the temperature gradient along the sample length, the ends of the cerium strips were shunted by thin silver foil so that the Joule heat was evolved mainly in the short (less than 3 mm in length) working part of the sample. Agreement between the average temperature of the working part of the sample and the magnitude of the electrical power supplied to it was established from the temperature dependence of the electrical resistance discontinuity at the transition $\gamma \rightleftarrows \alpha$, which was determined earlier in the piezometer heated in a tubular furnace as described above.

The pressure in this apparatus was determined by calibration using the electrical resistance discontinuities accompanying polymorphic transitions in the reference metals: bismuth, thallium, and barium which, according to Bridgman, [6] occur respectively at 25 × 10^3, 45 × 10^3 and 80 × 10^3 kg/cm^2 with rising pressure and approximately at 25 × 10^3, 28 × 10^3, and 60 × 10^3 kg/cm^2 with falling pressure.

Measurements on cerium No. 1 showed that the characteristic dependence R(p) described in earlier work [5,6] was considerably less marked at pressures above 30 × 10^3 kg/cm^2. In view of this we carried out studies at these high pressures using a sample with the same impurity content as that used by Vereshchagin et al. [5] [1)] The experimental curve for such cerium is shown in Fig. 2 in coordinates of the electrical resistance plotted against the press load. This figure shows also the press loads at which polymorphic transitions occurred in the reference metals on increase and decrease of pressure. These values may be useful for recalculation of our data using the "new"

[1)]Nominally that sample contained the following impurities (in %): 2 × 10^{-2} Fe, 1 × 10^{-3} Cd, 1 × 10^{-3} Pb, 1 × 10^{-3} Bi, 1 × 10^{-3} Sn, < 0.75 Nd, < 0.75 Pr, while cerium No. 1 contained 2 × 10^{-2} Fe, < 1 × 10^{-2} La, < 0.5 Nd, < 0.5 Pr.

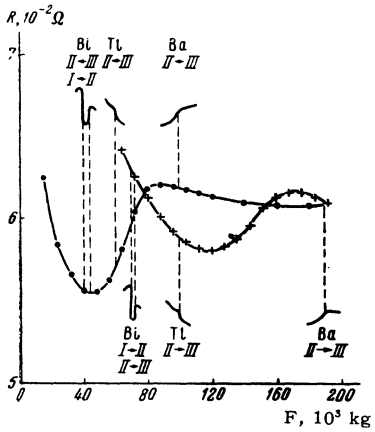

FIG. 2. Experimental curve of the dependence of the electrical resistance of cerium on the press load at 30°C: + – rising pressure; • – falling pressure. The dashed lines indicate press loads at which phase transitions were observed in bismuth, thallium and barium on increase and decrease of pressure.

scale of pressures plotted from rechecked values of the reference pressures.[8] If, after establishment of a constant pressure, the electrical resistance of cerium or of the reference metals drifted with time, measurements were carried out after a certain time interval. The magnitude of the time interval before the final reading was such that the rate of drift during that time fell by a factor of 10.

RESULTS OF MEASUREMENTS AND DISCUSSION

Figure 3 shows the piston piezometer results for the temperature dependence of the relative magnitude of the resistance discontinuity $\Delta R/R_\gamma$ at the $\gamma \rightleftarrows \alpha$ transition; here R_γ is the resistance of the sample in the γ-phase at a given temperature reduced to the points where the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ transitions begin. The phase diagram

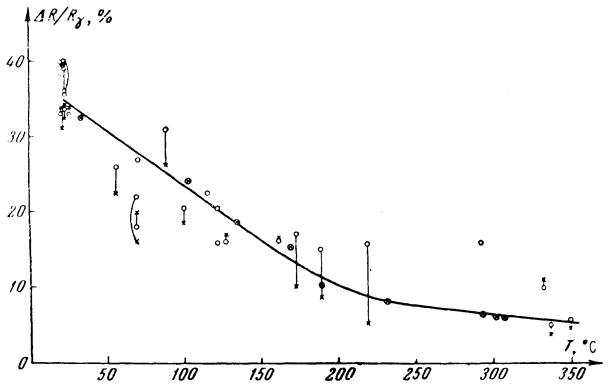

FIG. 3. Temperature dependence of the relative magnitude of the electrical resistance discontinuity for cerium No. 1: o – $\gamma \rightarrow \alpha$ transitions; × – $\alpha \rightarrow \gamma$ transitions. The experimental points for one test are joined by thin lines.

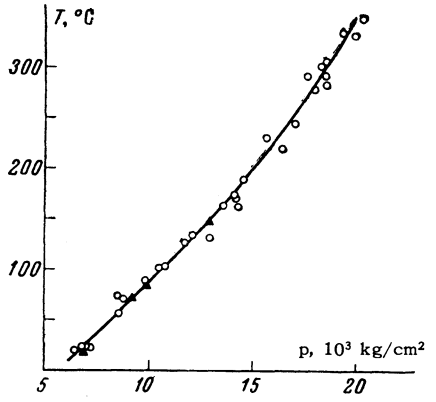

FIG. 4. Phase diagram of cerium No. 1: o – results obtained in the present work ▲ – results obtained by volume measurements.[7]

of cerium obtained in the present work for cerium No. 1 is given in Fig. 4.

Figure 3 indicates that the relative discontinuity of the electrical resistance falls from 32—40% at room temperature to about 10% at 200°C and in the range 200—350°C it decreases to 5—7%. These experiments included the region of the possible coordinates p and T of the critical point of the $\gamma \rightleftarrows \alpha$ transition of cerium, which according to various authors should occur in the range (18—20) $\times 10^3$ kg/cm^2 and 280—360°C[2)].

On the basis of direct measurements at temperatures corresponding to the known estimates of the critical temperature of the $\gamma \rightleftarrows \alpha$ transition we can say that in the quoted range of p and T values there is no continuous variation on transition from one isomorphic modification of cerium to the other. From the observation that up to 200°C the $\gamma \rightleftarrows \alpha$ transition pressures determined from the discontinuities of volume and of the electrical resistance are practically identical (Fig. 4), it follows that further along the (p, T)-boundary of the two phases the correlation between these parameters is retained, i.e., the volume and thermal changes remain finite up to 350°C. There is no basis for extrapolation of the high-temperature dependence $\Delta R/R_\gamma(T)$ to zero, especially since Figs. 3 and 4 show that at temperatures corresponding to the departure from the linearity of the dependence $\Delta R/R_\gamma(T)$ there is a change in the slope of the (p, T)-boundary between the re-

[2)]From thermal[3] and volume[4] measurements at high temperatures the coordinates of the critical point were estimated to be 18.5 × 10^3 kg/cm^2 and 280°C, 20 × 10^3 kg/cm^2 and 360°C, respectively. Linear extrapolation of the temperature dependence of the resistivities of the γ- and α-phases from low temperatures gave a critical temperature value $T_c = 315 \pm 15$°C.[1]

gions of existence of the γ- and α-phases[3)]. All the reported results indicate that the idea of the existence of a critical point is obviously wrong.

We should note that with increase of the transition temperature the sharpness of the discontinuity of the measured macroparameter (ΔV, ΔQ, ΔR) strongly decreases, i.e., the spread along the pressure scale becomes more marked. For this transition (in contrast, for example, to the transition Bi I $\rightleftarrows$ Bi II) there is a definite range of pressures at constant temperature in which both phases coexist. This greatly complicates detection of the transition at high temperatures at which also the absolute magnitude of the macroparameter discontinuity becomes quite small and may eventually make the transition completely unobservable. The authors of some of the cited papers [3,4] have obviously met this difficulty.

As reported earlier [3,7] and confirmed in the present work, the hysteresis of the transition decreases with increase of the transition temperature until it disappears completely; the hysteresis is defined as the difference between pressures at which the transitions $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ begin[4)]. Consequently the indeterminacy of the position of the true line of thermodynamic equilibrium of the two phases decreases at high temperatures. If one forgets the experimental difficulties mentioned in the preceding paragraph, then at high temperatures and with sufficiently accurate determination of the transition pressure the experimental "average line" (which has purely formal meaning) between (p, T)-values of the transitions $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ will become closer to the true equilibrium line. In this connection we may note that at lower temperatures the thermodynamic equilibrium line should shift to the "hot" threshold of the existence of the α-phase since it is known that in phase transitions of the first kind supercooling is, in general, more likely than superheating.

To elucidate the influence of temperature on the dependence R(p) for cerium at pressures up to 80×10^3 kg/cm^2, a series of R(p) curves was obtained for various values of the measuring current. One of such curves obtained at 30°C is shown in Fig. 2 and the results of ten experiments are condensed into the diagram of Fig. 5. The nature of the $\Delta R/R_\gamma = f(T)$ curve (Fig. 3) does not permit its use for estimating temperature above 200°C. Consequently the sample temperature above 200°C was estimated by linear extrapolation of the straight line T(W) which is valid if the proportionality between the temperature T and the power W, observed up to 200°C, is retained at higher temperatures. In estimating temperatures from the curve in Fig. 3 it is also assumed that the conditions of heat transfer existing at pressures of $(8-18) \times 10^3$ kg/cm^2 remain unaltered on increase of pressure to $(50-80) \times 10^3$ kg/cm^2. Although there are grounds for regarding these two assumptions as fully acceptable, the diagram of Fig. 5 is best regarded as qualitative. We should remember, however, that because of the weak temperature dependence of the pressures corresponding to the extremal points, an error of 50 or even 100 deg C in determination of temperature will not greatly affect the slope of the lines in the phase diagram.

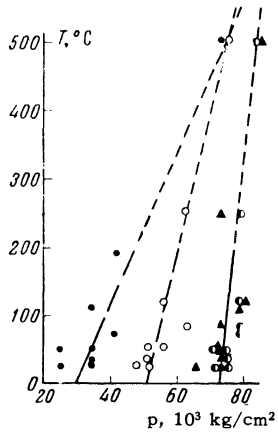

FIG. 5. (p, T) diagram of the positions of the maximum (▲, ●) and minimum (○, ●) of the electrical resistance of cerium: ●, ○ – rising pressure; ▲ ● – falling pressure.

Figure 2 shows that our series of experiments confirmed the existence of a minimum and a maximum on the R(p) curves for α-cerium, which were observed in earlier experiments at room temperature. [5,6] A qualitative similarity of the dependences R(p) of cerium and barium is noticeable in this range of pressures. According to our measurements (Fig. 5) the minimum and the maximum of the electrical resistance of cerium at room temperature occur respectively at pressures slightly higher than 50×10^3 and 70×10^3 kg/cm^2 when the pressure is rising; these values are in good agreement with the published data. [5,6] With falling pressure the value of p at the resistance minimum (p_{min}) is displaced to 30×10^3 kg/cm^2 and the pressure at the resistance maximum varies in the same way as the pressure of the transition Ba III → Ba II with respect to the pressure of the transition Ba II → Ba III. The

[3)] In Beecroft and Swenson's work[4] the experimental points in the plot of Fig. 2 also depart from the linearity of the (p, T)-boundary between the γ- and α-phases at temperatures of about 200°C. However, Beecroft and Swenson took no notice of this deviation and took it to be the result of experimental errors.

[4)] Obviously in the case when pressure applied directly to the sample is not measured this phenomenon is observed on the background of apparatus hysteresis.

magnitude of the pressure at the resistance maximum is, within the experimental error (the average scatter of pressure values in these tests was less than 6.5%), almost independent of temperature up to temperatures of the order of 500°C. With rising temperature the value of p_{min} is shifted toward high pressures and its hysteresis is reduced. As indicated by Fig. 5, the reduction in the hysteresis occurs mainly due to the shift of the "hot" threshold, i.e., of the values of p_{min} found with pressure decreasing. In the temperature range 25—200°C the relative change of the electrical resistance $(R_{max} - R_{min})/R_{min}$ at pressures of (50—60) $\times 10^3$ kg/cm^2 amounts on the average to about 10%. A detailed discussion of the results of our measurements suggests a tendency for decrease of this quantity on increase of temperature. In the purer sample (cerium No. 1) the magnitude of $(R_{max} - R_{min})/R_{min}$ amounts to only 6% at 25°C and the departures from the monotonic variation are clearly visible only when pressure is being reduced.

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