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HIGH-PRESSURE PHASE TRANSFORMATIONS IN CERIUM*

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compressibility

The X-ray diffraction method was used to study the volume change of the γ- and α-phases of cerium under the best equilibrium conditions and hydrostatic pressure of up to 10,000 kg/cm²: for the γ-phase $\Delta V/V_0 = 36 \times 10^{-7} p$; for the α-phase 88×10^{-7} $(p - p_0)$, where $p_0 = 1100$ kg/cm²; p is pressures ranging from 1100 to 10,000 kg/cm². In the range 1100-10,000 kg/cm² a hexagonal phase has been found and the lattice parameters, measured at $p = 6000$ kg/cm², are: $a = 3.671$ Å, $c = 11.700$ Å.

High-pressure phase change in cerium has been studied at low temperatures in [1-18]. The X-ray diffraction studies of [19-21] have shown that, like the original γ-phase, the high-pressure phase of cerium (α) has an f.c.c. lattice at high pressures and room temperature. But the lattice parameters are different in value.

Lawson and Tang [19] have found a lattice constant of $a_0 = 4.84 \pm 0.03$ Å for the α-phase at room temperature and $p = 15{,}000$ kg/cm² ($a_0 = 5.14$ Å for the γ-phase at room temperature and atmospheric pressure). The total volume change due to the γ-α transition is 16.5%. For the α-phase at room temperature and $p = 7000$ kg/cm², Adams and Davis in [20] found $a_0 = 4.824$ Å, total volume change 18%, change during transformation 14%. Yevdokimova and Genshaft in [21] found an α-phase at atmospheric pressure ($a_0 = 4.94$ Å).

X-ray diffraction analyses of cerium under high pressure [19-21] have not established the relation $\frac{\Delta V}{V_0} = f(p)$ where $\frac{\Delta V}{V_0}$ is the relative volume change of the material under a pressure p at constant temperature. Only Bridgman has found such a relation, by measuring the compressibility with the "piston displacement" method.

The problem in the present work was to study the relation between pressure and the relative volume change of cerium by means of X-ray diffraction analysis under the best equilibrium conditions.

EXPERIMENTAL PROCEDURE

The apparatus which we described in [22, 23] was used for X-ray diffraction analysis of cerium under high pressures. The size of the line focus was reduced to 12.0 × 0.2 mm by improving the focusing of the electron beam with a focusing X-ray tube [23]. Changes were made in the design of the beryllium compartment of the X-ray apparatus [22]: the special groove shown in Fig. 1, and the wall thickness of the compartment reduced from 3.3 to 1.5 mm at the groove. The groove was turned towards the collimator of the X-ray apparatus. The internal diameter of the cylindrical part of the compartment was 1.34 mm. Lithium

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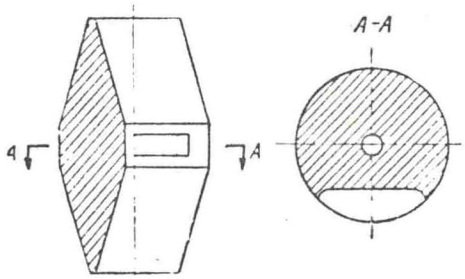

FIG. 1. Beryllium high-pressure vessel.

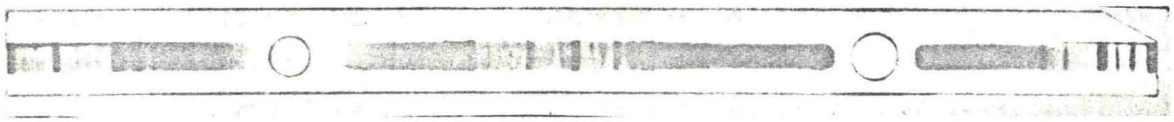

FIG. 2. Diffraction pattern of beryllium at a pressure of 9900 kg/cm^2.

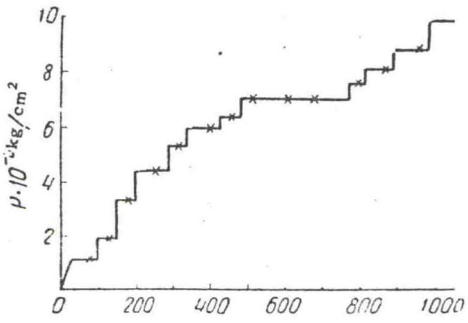

FIG. 3. Graph of cerium specimen held in apparatus under pressure (in one series of experiments); × - exposure time.

was used as the pressure transmitting medium.

The diffraction patterns were photographed in copper radiation at 40 kV and an anode current of 28 mA with 7-10 hr exposure (collimator aperature of 0.3 mm). A 0.016 mm aluminium foil was positioned in front of the film at the ring of the X-ray film holder; inside the collimator hood was a nickel filter 0.01 mm thick. The X-ray film was loaded asymmetrically into the holder (68.4 mm dia., Fig. 2); the effective radius of the camera was substracted for each photograph. 35 diffraction patterns were taken at high hydrostatic pressures of up to 10,000 kg/cm^2. To achieve the best equilibrium state the specimen was held at a certain

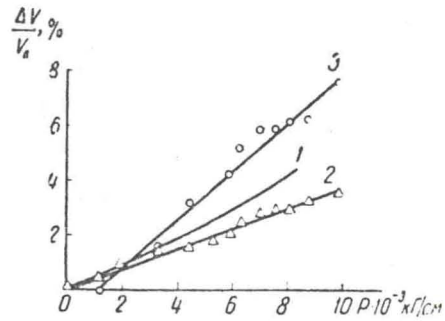

FIG. 4. Relative volume change of γ- and α-phases of cerium vs. pressure: (1) for γ-phase (according to Bridgman); (2) γ-phase (according to us); (3) for α-phase (according to us).

pressure for 10 hr before beginning the X-ray photography (Fig. 3). The pressure in the apparatus was measured within 2%; all the experiments were performed at 20 ± 2°C.

The cerium used in the experiments contained La < 0.01, Nd < 0.35, Pr < 0.35, Fe = 0.03%. The series of experiments described in this article were performed on a specimen in the shape of a cylinder 0.33 mm dia., which had been prepared by fine grinding with pure, dry vaseline oil as lubricant and coolant; no traces of asterism or texture were detected on the diffraction patterns.

RESULTS OF EXPERIMENTS AND CALCULATIONS

1. On the X-ray patterns taken in an RKU-114M (dia. 114.59 mm) at atmospheric pressure and room temperature only γ-Ce diffraction lines with indices (111), (200), (220), (311), (222), (400), (331), (420), (422), (511), and (333), (440), (531), (600) and (442), (620), (533), (622) were observed.

The lattice parameter was determined from reflections in the large-angle range (62-70°) with asymmetric arrangement of the film. Measurements and calculations produced a lattice constant $a_0 = 5.158 \pm 0.001$ Å. The same value was found at atmospheric pressure on diffraction patterns taken in the high-pressure apparatus.

On the diffraction patterns taken under high pressures were γ-phase lines with indices (111), (200), (220), (311), (222), (400), (331), (420), (422), (511) and (333), (440), (533), (622). On some of the patterns the $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$ doublet component lines (422) and (440) were resolved very well. We did not examine the cerium lines which almost coincide with either those of beryllium or lithium in this work.

To calculate the lattice parameter of γ-Ce at different pressures we used reflections from (311) and (222) planes as these were the best ones on all the diffraction patterns.

Bridgman's data, which were derived for γ-Ce by the "piston displacement" method (up to 7720 kg/cm²) can be used to describe the relation between $\Delta V/V_0$ and p in the form [24]

$$-\frac{\Delta V}{V_0} = 40{,}97 \cdot 10^{-7} p + 94{,}00 \cdot 10^{-12} p^2 + 4{,}53 \cdot 10^{-15} p^3. \quad (1)$$

According to our experimental results the analogous relation for the γ-phase of cerium may, up to p = 10,000 kg/cm², be given in the form

$$-\frac{\Delta V}{V_0} = 36 \cdot 10^{-7} p. \quad (2)$$

Equations (1) and (2) and the experimental data are shown graphically in Fig. 4.

2. Lines of the high-pressure phase of cerium (α-phase) were found on the pattern taken at p = 1100 kg/cm² (the photographs were started at this pressure); the lattice parameter of α-Ce was determined as $a_0 = 4.879 \pm 0.005$ Å, and taken as the start. The volume change of the γ-α transition was 15%.

The following reflections of α-phase planes were observed on the high-pressure diffraction patterns of cerium: (111), (200), (220), (311), (222), (400), (420), (422), (333) and (511), and of these the (420), (422), (333) and (511) lines were well resolved doublets on most of the patterns.

From the X-ray diffraction results we can give the $\Delta V/V_0 = f(p)$ relation for α-Ce as follows:

$$-\frac{\Delta V}{V_0} = 88 \cdot 10^{-7} (p - p_0), \quad (3)$$

where p_0 = 1100 kg/cm²; p is a series of pressures from 1100 to 10,000 kg/cm². This relation is shown graphically for α-Ce with the experimental points, in Fig. 4. The coefficients in equations (2) and (3) were determined by the least-squares method. The results obtained from the diffraction patterns and the corresponding calculations for the γ- and α-phases are shown in the Table.

3. In all the experiments in the pressure range 1-4000 kg/cm² a spontaneous increase in pressure was observed in the apparatus, and when diffraction patterns taken at 1100 kg/cm² and a series of pressures ranging up to 10,000 kg/cm² were analyzed, diffraction lines belonging to the hexagonal phase of cerium (β-Ce) were established. These lines have the following indices: (100), (101), (004), (102), (103), (104), (110), (114), (107), (008), (203) and (204). Both the experimental and calculated relative intensities of the reflections are qualitatively the same.

The a and c lattice constants determined from (104) and (111) lines of diffraction patterns taken at p = 6000 kg/cm² proved to be $a = 3.671 \pm 0.004$ Å, $c = 11.700 \pm 0.006$ Å. This pair of lines, which can be used to determine the lattice parameters, is the best for the hexagonal phase of all the diffraction patterns taken.

Some diffraction lines of α- and β-Ce consist of short separated streak reflections. This probably means that the phase transformation of γ- to α- and β-Ce begins in the larger grains.

Between 6300 and 7000 kg/cm² there was a big reduction in the amount of hexagonal phase and increase in the amount of α, but the hexagonal phase still coexists with γ- and α-phases at 10,000 kg/cm².

TABLE
Variation in lattice parameter of cerium under pressure.

p, kg/cm²	Lattice parameters a, Å	
	γ-phase	α-phase
1	5.158	–
1100	5.152	4.879
1900	5.143	not measured
3300	5.134	4.854
4400	5.133	4.867
5300	5.128	not measured
5900	5.123	4.809
6300	5.117	4.794
7000	5.112	4.782
7600	5.108	4.781
8100	5.107	4.777
8800	5.103	4.776
9900	5.098	4.754

Note. a determined within ± 0.005 Å.

CONCLUSIONS

1. The pressure dependence of the compressibility factor $\left[\varkappa = -\frac{1}{V_0}\left(\frac{\partial V}{\partial p}\right)_T\right]$ for the γ-phase differs according to whether it is derived from equation (1) or (2). According to Bridgman the compressibility factor γ-Ce rises with pressure, but according to our data it is not dependent on it, which means that the value of $\Delta V/V_0$ is a linear function of the pressure. This relation was found by Bridgman [26] in his first work on cerium, where only the compressibility of the γ-phase was measured because the transition to the α-phase was delayed by impurities. A linear relation between the pressure and relative volume change has also been found for the initial phase of cerium in [25].

The difference between our results and those of Bridgman [1-3] may be due to the fact that the piston displacement method which he used only measured the total volume change of the specimen due to the compressibility of the different phases of cerium and the changes in volume accompanying the phase transitions. Analysis of high-pressure diffraction patterns showed a γ-phase to exist in cerium at 10,000 kg/cm². The same was found in [13, 16, 21].

It is evident from Fig. 4 and equations (2) and (3) that the α-phase has higher compressibility than the γ. These conclusions are in contradiction with Bridgman's data [1-3] but are consistent with the results of [16, 21, 25].

2. It must be said that the β-phase detected in cerium in our experiments under pressure is probably the result of the experimental conditions, the rise and high level of hydrostatic pressure in the apparatus (Fig. 3). The hexagonal phase of high-pressure cerium was first discovered in the work by Lawson and Tang [19]. They said this phase appeared below the pressure of the γ-α transition but sometimes continued to exist at higher pressures. Those authors give neither lattice parameters nor indices of the diffraction lines in their work, and remark that the reproducrability of the phases was poor. The authors of [19, 20] apparently had a lower level of hydrostatic pressure in their apparatus, so that plastic deformation could occur in the cerium specimen, partially or completely suppressing the appearance of the

hexagonal phase.

McHargue and Yakel [9] have examined cerium by X-ray diffraction analysis in the range of temperatures from room to helium level, and they found that plastic deformation suppresses the γ-β transition; all the transitions covered a considerable range of temperatures.

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