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COMPRESSIBILITY OF CERIUM UP TO 30,000 kg/cm^2

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The pressure dependence of the volume decrement is found for two modifications of cerium, α-Ce and γ-Ce, by the "piston displacement" method and by x-ray diffraction. It is shown that the compressiblity of the gamma modification increases with pressure. By removing the pressure at a very gradual rate it is possible, at atmospheric pressure, to obtain the alpha modification with a lattice constant $a_0 = 4.94$ A.

A large number of papers on the compression of cerium have been concerned with explaining two interesting characteristics of this element, namely the possible existence of a critical point on the equilibrium curve in the $\alpha \rightleftarrows \gamma$ phase diagram and the anomalous behavior exhibited by the pressure dependence of the γ-Ce compressibility.

Bridgman found that at room temperature cerium undergoes a polymorphic transformation at pressures of about 7000 kg/cm^2 with an appreciable discontinuity in volume [1, 2]: he discovered when this happened that the compressibility of the γ-Ce low-pressure phase increased with pressure up to the transition point [2], which is an anomaly. The α-Ce high pressure phase behaves normally, i.e., its compressibility decreases with increasing pressure. Later it was demonstrated that this transformation is an isomorphic transition from the normal fcc phase to a phase with a collapsed fcc structure, where the lattice constant of the latter is $a = 4.84 \pm 0.03$ A at 15,000 kg/cm^2 [3]. An investigation of the phase diagram for cerium under pressure has established that the same transformation can be observed at atmospheric pressure in the low temperature region [4-6].

The special nature of this transformation, including the preservation of symmetry by the crystal lattice and the reduction in volume changes, heating effect, and changes in resistivity with increasing temperature and pressure of transition, has suggested the existence of a critical point on the $\alpha \rightleftarrows \gamma$ conversion curve [7-10]. However, in one of the more recent investigations devoted to the phase diagram of cerium it was shown that, although possible, such an occurrence is only faintly probable [11]. We note also that the cause of the $\alpha \rightleftarrows \gamma$ transition is assumed to be rearrangement of the outer electron levels, with one of the 4f-electrons going over to the 5d valence level [3]. This result was also confirmed by neutronographic investigation of the $\alpha \rightleftarrows \gamma$ transformation [12].

Considerably less attention has been devoted to the anomalous compressibility of γ-Ce. Bridgman's data, which he obtained in different years, imply inversion of the pressure dependences of the bulk compressibility of cerium [1, 13, 14].

Apart from Bridgman's work [1, 14], this anomalous behavior of γ-Ce has been further evidenced in x-ray studies at 15,000 kg/cm^2 [3] and ultrasonic measurements of the elastic moduli up to pressures of 10,000 kg/cm^2 [15].

The present paper is devoted to a study of the anomalous compressibility of gamma cerium using two alternative methods: the so-called "piston displacement" method and a method involving x-ray diffraction.

The apparatus used for the decrements ($\Delta V/V_0$) has been described in detail in earlier papers [8, 16]. The cerium sample[*] was compressed in a piezometer with lead used as the compressive medium. In the region of polymorphic transition we encountered certain difficulties in processing the data for the curve of "piston displacement vs. applied force" $\Delta l(F)$ insofar as the transition takes place in a certain pressure interval and is completed at

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[*] The samples were fabricated from material having the following impurities: Nd < 0.75%; Pr < 0.75%, Fe < 0.002%, Cd, Pb, Bi, Si < 10^{-3}%.

Variation of the Volume Decrements for Cerium, Calculated from Eq. (4) in [16] and Smoothed According to Eq. (1) of this Paper; Experimental Values

P, kg/cm²	$\Delta V/V_0$	
	Calc. from (4) [16]	Calc. from (1)
1	0.0000	0.0000
1000	0.0027	0.0033
2000	0.0071	0.0077
3000	0.0126	0.0132
4000	0.0190	0.0198
5000	0.0270	0.0275
10000	0.1672	
15000	0.1826	
20000	0.1985	
25000	0.2143	
30000	0.2291	

a point that is vague when the pressure is either raised or lowered. In processing our data we made a graphical normalization of the $\Delta l(F)$ curve to $F = 0$ and extrapolated according to the equation

$$-\left(\frac{\Delta V}{V_0}\right) = a\,(P - 1000) + b\,(P - 1000)^2, \qquad (1)$$

where P is in kg/cm², $a = 38.5 \times 10^{-7}$, $b = 55 \times 10^{-11}$.

The constant coefficients a and b were determined by the method of least squares from the experimental data, as described in [16]. It is clear that Eq. (1) is valid only to the transition point, i.e., for the gamma modification.

The accompanying table gives the experimental values of $(\Delta V/V_0)$ at 19°C, processed according to Eq. (4) of [16], and the values obtained by the smoothing process using Eq. (1) above and reduction to $(\Delta V/V_0) = 0$ at $P = 1$ atm.

For the x-ray investigations we used the camera described in [17]. A conical beryllium receptacle in this case took the part of the piston in a steel bomb. Slits were cut in the latter for the transmission of the x-radiation. The sample, in the shape of a very thin wafer 0.45 mm wide, was placed in an opening of the beryllium piston filled with dehydrated gasoline. The pressure was measured with a manganese manometer. Characteristic x-radiation from a molybdenum target was used during a 24-h exposure. As the pressure was increased, a series of lines typical of the high-pressure phase appeared on the x-ray diagram; under more or less ideal conditions eleven lines of the series could be distinguished against the background of the beryllium bands. Since the same film contained a photograph taken at atmospheric pressure we could calculate the relative change in volume with changing pressure for the gamma and alpha phases.

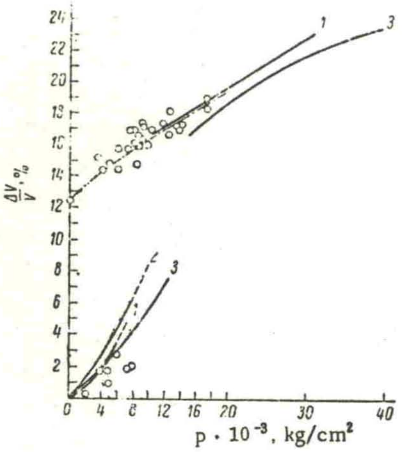

Fig. 1. Curves showing the variation of the volume decrement with pressure for the α- and γ-phases of cerium. 1) From our data, determined by the "piston displacement" method (the dashed curves were obtained by processing of the x-ray data represented by the circles of curve 1); 2) obtained by ultrasonic method [15]; 3) constructed from Bridgman's data, which were obtained by the "piston displacement" method [14].

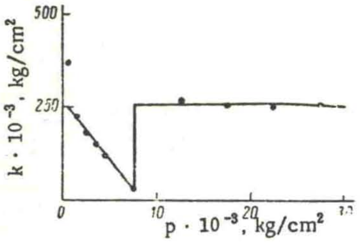

Fig. 2. Variation of the bulk compression modulus with pressure for α- and γ-cerium.

The results of our determination of $\Delta V/V_0$ are shown in Fig. 1, where the analogous dependences of $\Delta V/V_0 = f(P)$ obtained by other authors [14, 15] are also shown for comparison. It is evident that the compressibility data obtained in the present paper for the high-pressure phase of cerium using two alternative methods are in rather good agreement. As for the compressibility of the low-pressure phase, the piston displacement method bears out the anomalous variation with pressure. Figure

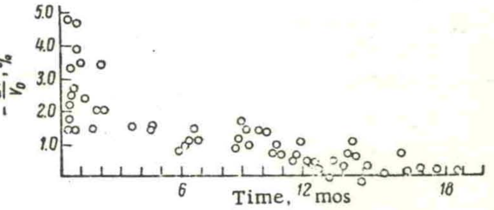

Fig. 3. Variation of the volume decrement of γ-Ce under a slow and gradual reduction of pressure down to atmospheric.

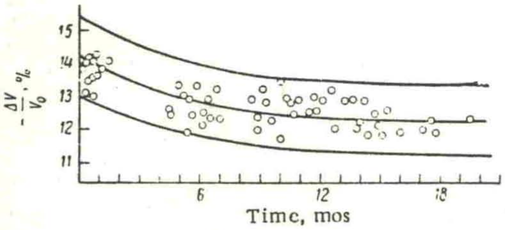

Fig. 4. Variation of the volume decrement of α-Ce under a slow and gradual reduction of pressure down to atmospheric. V_0 is the unit cell volume of α-Ce at 1 atm; $\Delta V = V_0 - (V_p)_\alpha$, where $(V_p)_\alpha$ is the unit cell volume of α-Ce at the pressure P.

2 shows the pressure dependence of the bulk compression modulus $k = -\frac{V}{\left(\frac{\partial P}{\partial V}\right)_T}$. The values of k were calculated from the formula $k = \frac{V_1 + V_2}{2} - \frac{P_2 - P_1}{V_1 - V_2}$; it is apparent that for the gamma phase of Ce the modulus k exhibits anomalous behavior as the pressure varies, while for all the other metals the bulk compression modulus increases. The x-ray data unfortunately do not permit any definite conclusions relative to the nature of the dependence $(\Delta V/V_0) = f(P)$.

One x-ray analysis showed that the initial phase of cerium tends to persist to pressure considerably in excess of the transition pressure 7000 kg/cm²; the presence of weak lines typical of this phase could be detected even at a pressure of 14,000 kg/cm². A similar lag in complete transformation was observed by Itskevich [10] at pressures of 10,000 kg/cm² and at room temperatures. It is necessary to point out that the high-pressure phase often persists down to very low pressures; when the pressure was lifted very gradually we found that the compact cubic phase remained in existence down to atmospheric pressure.

One case worthy of mention arose when the compact phase was created at atmospheric pressure. This happened as the result of lifting the pressure at an extremely slow rate (over a two-year period). In this experiment the beryllium pressure receptacle was forced tightly into the steel bomb and the cylindrical opening was filled with the sample. The quasi-hydrostatic pressure on the sample differed from the pressure in the bomb and was evaluated from the shift of the γ-phase lines relative to their positions at atmospheric pressure. After the piston was freed the pressure in the chamber was reduced to zero, while the pressure on the sample remained equal to 6000 mg/cm². The two-year observation of this sample showed that the pressure gradually dropped to zero, as is apparent from examination of Fig. 3. The graphical time dependence of the relative change in volume for the compact cubic α-phase was constructed from the x-ray photographs of this experiment. It is apparent from Fig. 4 that the curve approaches a value of 12.4%. Hence it is possible to produce the lattice constant of the collapsed fcc form of cerium at atmospheric pressure. This constant turns out to be equal to 4.94 A.

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