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Elastic properties of cerium at pressures up to 84 kbar and at a temperature of 293 K

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The elastic properties of polycrystalline cerium have been studied by the ultrasonic method under conditions of quasihydrostatic pressures up to 84 kbar at a temperature of 293 K. The pressure dependence of the density, elastic bulk modulus, shear modulus and Debye temperature were determined from the data obtained on the velocities of propagation of longitudinal and transverse ultrasonic waves. An anomalous change in a number of elastic characteristics were observed, connected with the γ–α (7.5 kbar) and α–α' (51 kbar) phase transformations. The singularities of the change in the elastic properties of the α- and α'- phases of cerium point to a structural character of the α–α' transformation. It follows from an estimate of the dependence of the density on the pressure that the most probable structure of the α'- phase of cerium is orthorhombic of the α- uranium type. A softening of the longitudinal acoustical modes was observed upon approach to the electronic γ–α transition and a softening of the transverse acoustical modes upon approach to the structural α–α' transformation. The softening of the phonon spectrum of cerium found at high pressures correlates with the superconductivity phenomenon, and explains also the singularities of the melting curve of cerium in correspondence with Lindemann's representations.

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At high pressures, cerium exhibits a number of interesting properties, due to a change both in the electronic states and in the symmetry of the lattice. The anomalous increase in the compressibility of the γ phase of cerium with pressure is well known, as is the jumpwise decrease in the volume of the face-centered curbic (FCC) lattice by 14% at 7.5 kbar.[1] It has been shown that the localized $4f$ electron goes in this case to the sd conduction band,[2] and the magnetic FCC (the γ phase of cerium) goes over into the nonmagnetic FCC (the α phase).[3] The equilibrium line of the γ–α transformation terminates at the critical point.[4] It follows from measurements of the Hall effect[5] that the number of $4f$ electrons decreases by 0.6–0.8 in the γ–α transition, while the valence changes from 3.06 ± 0.06 to 3.67 ± 0.09.[6] It has been suggested[1] that further compression increases the valence of α-Ce to 4.0; however, neutron diffraction analyses[7] have shown that the $4f$ electron becomes delocalized already at 8 kbar.[8] At 51 kbar, as was noted from the jump in the electrical resistance,[9] α-Ce transforms into α'-Ce; the equilibrium line of this transformation was determined in Ref. 10. It was found that α'-Ce is superconducting.[8,11] On the basis of x-ray investigations, various structures were proposed for the α'-phase: FCC,[12] slightly distorted HCP,[13] orthorhombic of α-uranium type,[1] HCP,[14] and correspondingly various volume discontinuities in the α–α' transition. X-ray structure in investigations up to 175 kbar[15] have shown the existence of a tetragonal phase of cerium above 120 kbar; however, the structure of the α' phase was not interpreted in that work. The sharp change in the slope of the plot of the electrical resistance of cerium on the pressure in this transition has been proposed as a reference point of the pressure scale.[16]

There is undoubted interest in the study of the propagation velocity of elastic waves in cerium over a wide range of pressures. These reflect the changes in the low-frequency acoustic part of the phonon spectrum and determine the elastic characteristics of the high pressure phases and the features of their change as a result of phase transitions.

The elastic characteristics of cerium were studied by us previously up to 9 kbar,[17] and we first observed the strong softening of the longitudinal acoustic modes near the γ–α transformation.

For the present experimental investigations, we used polycrystalline cerium of grade TseM-1 with content of the basic ingredient 99.93%, of grade Ce É-1 (99.53%), and cerium of purity 99.95% obtained from the CNRS

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laboratory of rare earths (France). At atmospheric pressure and a temperature of 293 K, we determined the values of the propagation velocities of longitudinal ($v_{l,0}$) and transverse ($v_{t,0}$) ultrasonic waves. The values used for calculations, $v_{l,0} = 2283$ m/sec and $v_{t,0} = 1350$ m/sec, were obtained with the TseM-1 samples and differ from the velocity values in Ce É-1 and Ce (CNRS) by 3% on average.

The investigation of the elastic properties of cerium at high pressures was carried out in two stages. In the pressure range 0–20 kbar, the measurements were carried out on apparatus of the piezometric type, i.e., under quasihydrostatic conditions by the method described in Ref. 18, on samples of grades TseM-1 and Ce É-1. The diameter of the samples was 20 mm, height 7–10 mm. During the course of experiments, the change of the times of flight of longitudinal $[\Delta t_l(p)]$ and transverse $[\Delta t_t(p)]$ ultrasonic waves with pressure was determined, and also the change in the height $[\Delta l(p)]$ of the samples. It should be noted that no effect of the purity of the samples on the measured dependencies was observed within the limits of accuracy of the experiment.

The $\gamma-\alpha$ phase transition in cerium was characterized by a sharp and simultaneous change in the character of the $\Delta t(p)$ and $\Delta l(p)$ dependences. Upon increase in pressure, the $\gamma-\alpha$ transition set in at $p = 7.5 \pm 0.2$ kbar. When the pressure was decreased, the reverse $\alpha-\gamma$ transition was observed at $p = 5.7 \pm 0.2$ kbar. Thus the hysteresis of the phase transformation in these experiments amounted to 1.8 ± 0.2 kbar. The value of the volume jump in the $\gamma-\alpha$ transition $\Delta V/V = (13.45 \pm 0.13)\%$ was found from measurements of the $\Delta l(p)$ dependence with account taken of the deformation of the chamber. This value is in excellent agreement with the latest data in the literature.[1,19] The results of six experiments for the determination of the dependence $v_l(p)$ and five such experiments for $v_t(p)$ were used in the calculation.

The measurements in the range 20–84 kbar were carried out on high pressure apparatus[20] according to a method described earlier,[21] on samples of three grades of cerium. The length of the samples was 6 mm, the diameter 14 mm. During the experiments, the change with pressure of the time of flight of longitudinal $\Delta t_l(p)$ and transverse $\Delta t_t(p)$ ultrasonic waves and the height of the sample $l(p)$ were measured. Corrections to the measured values because of the deformation of the chamber were determined in a special series of experiments. The results of the measurements on the samples of the three grades were identical within the limits of error of the experiments. The pressure in the chamber was determined for each experiment from the jumps in the electrical resistance of the reference metals Bi, Tl, and Ba. The values of the transition pressures were assumed in correspondence with Ref. 22. The sharp disruption of the monotonic dependences $\Delta t_l(p)$ and $\Delta t_t(p)$ enabled us to record the beginning of the $\alpha-\alpha'$ transformation in cerium, and to assume the transition pressure to be $p = 51 \pm 1$ kbar. For calculation of the dependences $v_l(p)$ and $v_t(p)$ in the interval 20–84 kbar, we used the results of six and five experiments, respectively, in sections of rising pressure. As initial data for this calculation, we used the values of v_l and v_t at 20 kbar, obtained with the piezometric apparatus.

The $v_l(p)$ and $v_t(p)$ dependences were used for the calculation of the density $\rho(p)$, the elastic bulk modulus $K_s(p)$, the shear modulus $G(p)$, and the Debye temperature $\Theta(p)$ in the pressure range 0–84 kbar. The calculation was carried out in correspondence with the expressions given in Ref. 23. The adiabatic-isothermal correction was calculated at values of the thermal expansion coefficient $\alpha = 2.58 \times 10^{-5}$ deg^{-1} and specific heat $c_p = 0.1932$ J/g-deg[24] and was assumed to be constant in view of the absence of data on the $\alpha(p)$ and $c_p(p)$ dependences for cerium. The values of the calculated elastic characteristics and the density of cerium for the pressures 0–84 kbar are given in the Table.

Figure 1 shows the $v_l(p)$ and $v_t(p)$ dependences for the pressure range 0–84 kbar. A characteristic feature of the γ phase of cerium is the progressive decrease in the velocity of the longitudinal wave upon approach to the $\gamma-\alpha$ transformation point. This indicates a significant softening of the long-wave longitudinal modes in the phonon spectrum of γ cerium. This fact and the increase in the velocity of the longitudinal waves in the $\gamma-\alpha$ transition are connected with the shift rearrangement oc the localized $4f$ level relative to the Fermi level upon compression. Account of the hybridization of the f electrons with the conduction electrons made it possible to

TABLE I. Elastic properties of cerium at pressures up to 84 kbar and temperature 293 K.

p, kbar	v_l, m/sec	v_t, m/sec	ρ, g/cm^3	K_s, kbar	G, kbar	Θ, K
			γ-Ce			
0	2283	1350	6.775	188.5	123.5	137.0
2	2226	1350	6.851	173.0	124.8	137.2
4	2146	1350	6.936	150.9	126.4	137.3
6	2014	1350	7.041	114.5	128.3	136.9
6.6 *	1966	1350	7.080	101.6	129.0	136.7
			α-Ce			
6.6 *	2096	1443	8.180	132.3	170.5	153.3
8	2200	1446	8.256	169.4	172.6	155.0
10	2298	1450	8.345	206.7	175.4	156.7
20	2528	1469	8.676	304.8	187.2	162.2
30	2649	1481	8.939	365.9	196.1	165.7
40	2690	1438	9.172	411.0	189.5	162.8
42	2688	1421	9.216	417.8	186.1	161.3
44	2684	1401	9.260	424.8	181.8	159.4
46	2679	1377	9.304	432.5	176.4	157.1
48	2671	1348	9.346	440.4	169.8	154.2
50	2667	1318	9.389	450.3	163.1	151.2
51	2664	1302	9.409	455.1	159.5	149.5
			α′-Ce			
51 *	2716	1247	9.512	504.5	147.9	144.2
52 *	2758	1266	9.531	521.3	152.8	146.4
54 *	2832	1302	9.567	551.0	162.2	150.8
56	2900	1338	9.600	578.2	171.9	155.2
58	2946	1375	9.634	593.2	182.1	159.5
60	2973	1398	9.666	602.5	188.9	162.3
62	2983	1418	9.698	603.0	195.0	164.7
64	3008	1436	9.730	612.7	200.8	167.0
66	3045	1453	9.762	630.3	206.1	169.1
68	3081	1469	9.793	647.8	211.3	171.2
70	3114	1483	9.823	664.5	216.0	173.0
72	3146	1497	9.852	680.7	220.8	174.8
76	3194	1520	9.910	705.7	229.0	177.8
80	3220	1542	9.966	717.3	237.0	180.7
84	3236	1560	10.021	724.4	243.7	183.0

*These values of the elastic characteristics were obtained upon extrapolation of the measured values to the average transition pressure in the case of $\gamma-\alpha$ transformation and to the transition pressure on the direct path in the case of an $\alpha-\alpha'$ transformation.

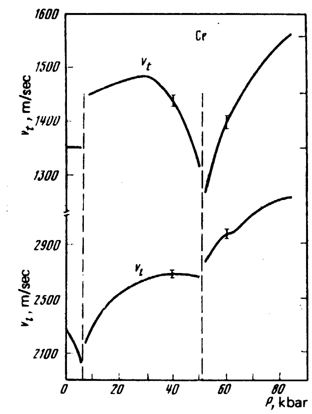

FIG. 1. Dependence on pressure of the propagation velocities of longitudinal v_l and transverse v_t ultrasonic waves in polycrystalline cerium.

explain the presence of a minimum in the $v_l(p)$ dependence in the $\gamma-\alpha$ transition of cerium.[25] Physically this minimum is connected with the increase in the screening of the ion-ion interaction when the f electrons go through the Fermi surface. The progressive decrease in the velocity of the longitudinal waves and the elastic bulk modulus as the phase boundary of the isomorphic $\gamma-\alpha$ transformation is approached is similar to the behavior of these characteristics as the liquid-vapor equilibrium line is approached;[26] it terminates at the critical point, where $(\partial p/\partial V)_T = 0$. Similarly,[26] for cerium one should expect still further softening of the longitudinal modes in the phonon spectrum with increase in temperature and pressure upon approach to the critical point.

The transition from the γ to the α phase is accompanied by a significant increase in the elastic characteristics. In the range 7.5–30 kbar, all the elastic characteristics of the α-phase of cerium increase with pressure. At $p = 30$ kbar, $v_t(p)$, $G(p)$ and $\Theta(p)$ pass through a maximum (Figs. 1 and 2) and then fall off appreciably as the $\alpha-\alpha'$ transformation is approached. This decrease indicates an ever increasing instability of the α-Ce lattice to shear strains that lead to the structural $\alpha-\alpha'$ transformation, which was observed by us at $p = 51 \pm 1$ kbar. The singularities of the behavior of $v_t(p)$, $G(p)$ and $\Theta(p)$ of α-cerium qualitatively repeat the picture obtained for the pretransitional region in BaI.[21] The monotonic, singularity-free increase in the elastic bulk modulus $K_s(p)$ for α-cerium, in contrast to the behavior of this modulus in the γ-phase as the electronic $\gamma-\alpha$ transition is approached, also indicates the structural character of the $\alpha-\alpha'$ transformation.

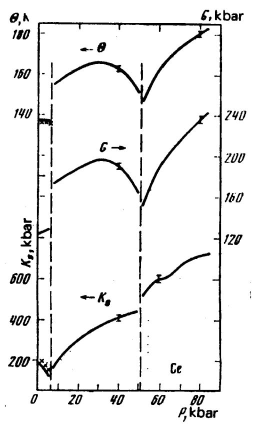

FIG. 2. Pressure dependence of the elastic bulk modulus K_s, the shear modulus G, and the Debye temperature Θ for polycrystalline cerium; ×—Ref. 17.

The decrease in the velocity of shear waves and the increase in the elastic bulk modulus at $p > 30$ kbar point similarly[21] to a softening of the transverse modes TA1 and TA2 with pressure in the phonon spectrum of α-cerium. The decrease in the stability of the simple face-centered cubic lattice of α-cerium in compression is evidently due to the change in the electron spectrum and its contribution to the shear constants $(c_{11} - c_{12})/2$ and c_{44}.

The $\alpha-\alpha'$ phase transition in cerium is accompanied by a jumpwise decrease in the velocity of transverse and an increase in the velocity of longitudinal ultrasonic waves. Both velocities increase with pressure in the α'-phase. For calculation of the change in density with pressure and subsequently the elastic characteristics, it was necessary to choose a reasonable value of the density jump in the $\alpha-\alpha'$ transition. In the case of the γ-α transformation, we used the value of $\Delta V/V$ from our measurements with the ultrasonic piezometer. The value of the jump $\Delta V/V$ could not be determined in experiments in the range 20–84 kbar. From x-ray measurements, various values of $\Delta V/V$ in the $\alpha-\alpha'$ transformation were determined, depending of the chosen structure for the α' phase: 7%,[14] 4.3%,[12] and 1.1%.[1] We calculated (up to 84 kbar) the change with pressure of the density of α'-cerium using the indicated jumps, and the dependence $\rho(p)$ was extrapolated into the region of existence of the tetragonal phase ($p > 121$ kbar).[15] As is seen from Fig. 3, only the use of the quantity $\Delta V/V = 1.1\%$ leads to agreement of the extrapolated $\rho(p)$ with the experimental data.[15] The fact that we did not record anomalies in the $\rho(p)$ dependence in the case of cerium also points to a small (1.1%) change in the density of cerium in the $\alpha-\alpha'$ transformation, whereas the same measurement method revealed a change in the length of the sample in the phase transition BaI–BaII with a volume jump $\Delta V/V = 2.8\%$.[21] We can thus conclude that the most probable structure of the α'-phase of cerium is the orthorhombic type α-U. This same conclusion was reached in a recently published work,[27] in which the volume jump of cerium at 51 kbar was determined from volume measurements and amounted to $(1.5 \pm 1)\%$.

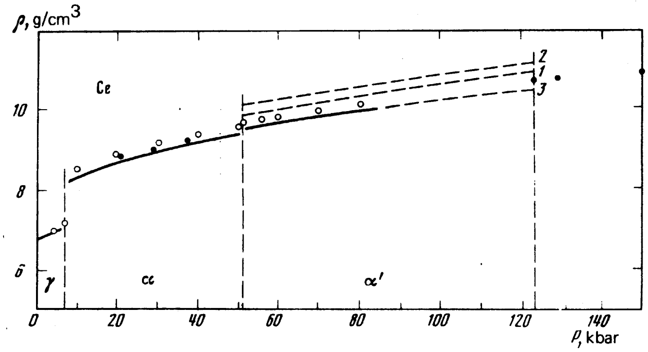

FIG. 3. Pressure dependence of the density of polycrystalline cerium. The solid line represents our data; the dashed lines are the result of calculation from our data with account of $\Delta V/V$ in the $\alpha - \alpha'$ transition; 1—Ref. 12, 2—Ref. 14, 3—Ref. 1; ○—Ref. 1; ●—Ref. 15.

The elastic bulk modulus, the shear modulus, and the Debye temperature of α'-cerium increase with pressure. In the dependence of the velocity of longitudinal waves on the pressure, a singularity was repeatedly noted in experiments on various samples—a small minimum at a pressure of 62 kbar. The value of the minimum exceeds the error of the relative measurements of the sound velocity (the probable errors of measurement of the absolute values are shown in Figs. 1 and 2). It is possible that this singularity is connected with an α'' phase of cerium, observed in this range of pressures.[1]

It is interesting to observe that the softening of the phonon spectrum of cerium at high pressures that we observed experimentally correlates with the appearance of superconductivity of cerium and with the dependence of T_c on the pressure. The onset of superconductivity of γ-cerium prevents the presence of a localized $4f$ electron. The softening of the transverse acoustical modes of α-cerium above 30 kbar and the progressive character of this phenomenon apparently occur also at low temperatures and lead to the onset of superconductivity of this phase above 20 kbar[8] and an increase of $T_c \sim \langle \omega^2 \rangle^{-1}$ with pressure. The jumpwise increase in T_c in the $\alpha-\alpha'$ transition correlates with the stepwise decrease in the velocity of the transverse waves. The increase in the velocity of ultrasound in the α' phase corresponds to a decrease in T_c upon further compression of the cerium.[11]

The softening of the acoustical modes observed in the phonon spectrum of γ- and α-cerium explains in conjunction with the representations of Lindemann, the singularities of the phase diagram of cerium: the negative slope of the melting curve, the minimum of which coincides with the extension of the boundary of the α-α' phases. Further increase in the melting temperature corresponds to an increase in the elastic characteristics of the α' phase with pressure.

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