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PHYSICS

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EFFECT OF HYDROSTATIC PRESSURE ON THE ELASTIC PROPERTIES OF CERIUM

Cerium is known for anomalies in its properties at high pressures and low temperatures.

A. I. Likhter, Yu. N. Ryabinin, and L. F. Vereshchagin (⁀1) showed that the abrupt changes in the volume of cerium found by P. Bridgman at $p = 7600$ kg/cm^2 and $T = 30°$C (⁀2), and by Trombe and Foex at low temperatures (⁀3), are the consequence of one and the same first-order polymorphic transition, in which, according to the investigations of Lawson and Tang (⁀4), the face-centered cubic lattice existing at room temperature and atmospheric pressure, with $a = 5.14$ Å (γ-cerium), while being preserved under pressure, changes its parameter discontinuously to 4.84 Å (α-cerium). Leipfinger (⁀5), on the basis of his measurements, suggested that in this process cerium undergoes a transition from the paramagnetic state to an antiferromagnetic one.

The anomalies of the properties of γ-cerium—an increase in compressibility (⁀6) and a rise in electrical resistivity (⁀7) with increasing pressure, as well as a negative temperature coefficient of volume expansion (⁀8)—disappear upon transition to the α-phase.

We investigated the elastic properties of cerium under high hydrostatic pressure and their change during the polymorphic transition by an ultrasonic method. The propagation velocities of ultrasonic waves were measured with a pulsed apparatus (⁀9), connected “in transmission”(Fig. 1), in which, for measurements in cerium, a carrier frequency of 3.5–5.5 MHz was used, along with a more precise circuit for smooth delay of the oscilloscope triggering; the scatter of calibration points over the 5-megahertz sine wave of the quartz-stabilized generator was ± 0.01 μs.

From cerium castings with the following composition: Ce 98.5%; rare-earth elements 1.5%; Fe 0.002%; Pb, Bi, Sn, Sb 0.00(3)%, samples 20 mm in diameter and of various lengths were cut out. After annealing (24 hours in vacuum $p =$

10^{-4} mm, $T = 500^{\circ}$C) the ends of the samples were lapped to a deviation from parallelism of less than 0.01 mm. The density was determined by hydrostatic weighing in absolutized benzene and was found to be 6.775 g/cm^3.

A sample with glued-on quartz plates was placed in a high-pressure vessel (Fig. 1). With the aid of a multiplier, hydrostatic pressure was produced in the vessel; it was measured with a class 1 spring manometer for 10,000 kg/cm^{-2}, calibrated before and after the experiments against an absolute piston manometer ($\frown$10) with an accuracy of ± 25 kg/cm^2. All measurements were carried out at a temperature of $16.0 \pm 0.1^{\circ}$C. By changing the pressure by Δp, the displacement of the pulse that had passed through the sample, caused by the change in pressure, was compensated on the oscilloscope screen by means of a smooth sweep-trigger delay, and thus the corresponding Δt—the change in the transit time of the ultrasonic waves—was determined. The pressure was increased or decreased on the reverse run in steps of 500 kg/cm^2, closer to the phase-transition point in steps of 200 kg/cm^2, and in the immediate vicinity of the transition in steps of 50 kg/cm^2.

When approaching the phase-transition region from the side of low or high pressures, high stability of the readings was observed; after the transition, to achieve reproducibility of the readings at constant pressure, a considerable holding time was required, decreasing with distance from the transition region.

In all experiments the phase transition began, upon increasing the pressure, at 7650 ± 50 kg/cm^2, and upon decreasing it—at 5950 ± 50 kg/cm^2, and was recorded as a continuous change in the transit time of ultrasonic waves in the specimen at constant pressure by a considerable amount; this ended after 1.5–2 hours.

The change in the transit time of longitudinal ultrasonic waves in cerium with pressure was determined in 4 experiments on a specimen 12.29 mm long and in 2 experiments on a 16.65 mm specimen, the results of which were recalculated to the length 12.29 mm. The study of the transit time of transverse waves was carried out in 5 experiments; in 4 of these, the bond between the quartz plate and the specimen was destroyed during the phase transition, and only in one experiment was it possible to carry out measurements after the transition and on the reverse path.

For calculating the elastic characteristics of cerium under high pressure, portions of the dependences $\Delta t = f(p)$ before the phase transition from 0 to 7650 kg/cm^2 and from the maximum pressure 9500 kg/cm^2 to the onset of the reverse transition, 5950 kg/cm^2, smoothed by first and second differences, were used, i.e., portions of stable readings. The calculation was performed for pressures 1; 500; 1000; 1500 kg/cm^2, etc. For the n-th pressure step the adiabatic bulk modulus was determined as

$$K_{s,n} = l_n^2 \rho_n \left[(t_{l,0} + \Delta t_l)^{-2} - \frac{4}{3}(t_{t,0} + \Delta t_t)^{-2} \right], \tag{1}$$

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

where $t_{l,0}$ and $t_{t,0}$ are the transit times of longitudinal and transverse ultrasonic waves in a cerium specimen of length l_0, calculated from the corresponding ultrasonic velocities $v_{l,0} = 2300$ m/sec and $v_{t,0} = 1330$ m/sec at atmospheric pressure (^{11}). The adiabatic bulk modulus was converted to the isothermal one,

$$K_{T,n} = \frac{K_{s,n}}{1 + \dfrac{\alpha^2 T K_{s,n}}{\rho c_p}}, \tag{2}$$

where α is the coefficient of volumetric thermal expansion, equal to $2.58 \cdot 10^{-5}$ deg^{-1} (^{12}); c_p is the heat capacity at constant pressure, equal to 0.05 cal/g$\cdot$deg (^{13}). Their variation with pressure was neglected because of their weak dependence on pressure and the smallness of the correction for isothermality.

The product $l_n^2 \rho_n$ was determined from the values of $l_{n-1}^2 \rho_{n-1}$ of the preceding calculation step, taking into account their change with increasing pressure by the method of successive approximations:

$$l_n^2 \rho_n = l_{n-1}^2 \rho_{n-1} \left(1 + \frac{1}{3} \frac{\Delta p}{\overline{K}_{T,n}}\right), \qquad \Delta p = 500 \text{ kg/cm}^2,$$

$$\overline{K}_{T,n} = \frac{1}{2}\left(K_{T,n-1} + K_{T,n}\right). \tag{3}$$

Fig. 1. Block diagram of the apparatus.
1 —trigger unit; 2 —pulse generator; 3 —USh-10 amplifier; 4 —IO-4 oscilloscope; 5 —obturator; 6 —obturator nut; 7 —high-pressure vessel; 8 —electrodes; 9 —piezoelectric transducer; 10 —cerium specimen; 11 —piezoelectric receiver.

In the first approximation $K_{T,n} = K_{T,n-1}$; in the second and subsequent approximations $K_{T,n}$ was obtained from $K_{s,n}$, calculated by formulas (1, 2). The values of $K_{s,n}$ in the third approximation practically coincided with $K_{s,n}$ in the second approximation and were regarded as final.

Fig. 2. Dependence of the propagation velocities of longitudinal (v_l) and transverse (v_t) ultrasonic waves and of the Debye temperature θ_D on hydrostatic pressure p for cerium

Fig. 3. Dependence of the elastic properties of cerium on hydrostatic pressure

Next, the shear modulus, Young's modulus, Poisson's ratio, and the propagation velocities of longitudinal and transverse ultrasonic waves were calculated:

$$G_n = l_n^2 \rho_n (t_{t,0} + \Delta t_t)^{-2}; \tag{4}$$

$$E = \frac{3K_{s,n}}{A-1}, \qquad A = \frac{v_l^2}{v_t^2} = \frac{(t_{t,0} + \Delta t_t)^2}{(t_{l,0} + \Delta t_l)^2}; \tag{5}$$

$$\sigma = \frac{1}{2}\frac{A-2}{A-1}; \tag{6}$$

$$v_n = l_n (t_0 + \Delta t)^{-1}, \qquad l_n = l_{n-1}\left(1 - \frac{1}{3}\frac{\Delta p}{K_{T,n}}\right). \tag{7}$$

The characteristic temperature was determined from the Debye-Einstein relation, reduced to a form convenient for calculations:

$$\theta_{D,n} = \frac{h}{k}\left(\frac{9N_a}{4\pi}\right)^{1/3} l_0 \left(\frac{\rho_0}{M}\right)^{1/3} \left[(t_{l,0} + \Delta t_l)^3 + 2(t_{t,0} + \Delta t_t)^3\right]^{-1/3}, \tag{8}$$

where h and k are the Planck and Boltzmann constants, N_a is Avogadro' s number, and M is the molecular weight.

The calculation of the elastic properties of the cerium specimen that underwent the polymorphic transition ($p = 6000 \div 9500$ kg/cm^2) was carried out in an analogous manner. The magnitudes of the jumps in the elastic properties at the phase transition were calcu-

calculated from the measured values of Δt_l and Δt_t, and also Δl and $\Delta \rho$, determined from the value of $\Delta V/V_0$ for the transition, equal to 8% ([7,14]).

The results of the calculation are presented in Figs. 2 and 3. On the same graphs the probable error in the values of the elastic characteristics is plotted, caused by an error of ±0.02 μsec in the determination of Δt_l and Δt_t before the transition and ±0.02 μsec for Δt_l and ±0.05 μsec for Δt_t after the phase transition.

The ultrasonic investigation, carried out for the first time, of the first-order phase transition and the elastic properties of cerium under high pressure showed that anomalies of the elastic properties are inherent in the γ phase of cerium and disappear upon transition to the α phase. Before the transition, Young' s modulus, the bulk modulus, and Poisson' s ratio decrease with increasing pressure.

The increasing curvature of these dependences apparently indicates a progressive weakening of the interatomic bonds as the phase transition is approached.

The Debye temperature, which characterizes the quasi-elastic force of interatomic interaction, passes through a maximum and decreases toward the transformation point.

The first-order phase transition in cerium was accompanied by an increase in the values of the elastic characteristics by a finite jump, with the exception of Poisson' s ratio, whose dependence on pressure undergoes a kink. The hysteresis phenomena found in ultrasonic studies of the phase transition in cerium correspond to those found earlier in electrical ([7,15]) and volume measurements ([6,15]), and are apparently inherent in the process of restructuring of the crystal lattice itself and are not connected with the methods used to study the phase transition.

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