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ELASTIC PROPERTIES OF BARIUM AT PRESSURES UP TO 22 000 kg/cm^2

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The pressure dependence of the longitudinal and transverse wave velocities in barium was investigated by an ultrasonic pulse method up to 22 000 kg/cm^2. The pressure dependences of the density of barium, the bulk moduli, Young's modulus, the shear modulus, Poisson's ratio, and the Debye temperature were calculated. The presence of a phase transition [3,4] at 17 500 kg/cm^2, with a volume discontinuity $\Delta V/V_0 = 0.5\%$, was confirmed.

THE present study is an extension of the investigations [1,2] of the elastic properties of solids, by an ultrasonic pulse method, to a wider range of pressures. An investigation of the elastic properties of barium is of interest because of its high compressibility, compared with the metals investigated earlier, and the anticipated correspondingly large effects and nonlinearity of the variation of its elastic properties with pressure.

It was also interesting to determine the pressure dependence of the compressibility of this metal using an ultrasonic method, and to compare this dependence with the compressibility data of Bridgman, who established, at 17 000 kg/cm^2, a phase transition with a volume discontinuity of 0.6% and a resistance discontinuity of 0.35%.[3,4] Investigations of the phase diagram of barium by differential thermal analysis,[5] x-ray structure investigations,[6] and an investigation of the electrical resistance of barium [7] at various pressures and temperatures have failed to confirm the existence of a phase transition at 17 000 kg/cm^2. Using ultrasonic measurements [8], one can determine quite accurately changes in the elastic properties of a substance, in particular the bulk modulus, and calculate the pressure dependence of the density.

In the investigation, we used barium containing 99.99% Ba, 0.005% Fe, 0.0004% Zn, 0.0003% Pb, 0.0003% Cr, 0.0016% Cu, 0.00018% Cd. Blanks were cut from an ingot, and working samples—20 mm in diameter and 5 to 15 mm high—were extruded from the blanks at a pressure of 20 000 kg/cm^2. During their preparation and storage, the samples were protected from oxidation by a layer of degassed oil. The values of the longitudinal and transverse wave velocities were determined for these samples at atmospheric pressure and 25°C: $V_{l0} = 2235 \pm 3$ m/sec and $v_{t0} = 1325 \pm 4$ m/sec. From the values of the zero-pressure velocities and density, we determined the elastic properties of barium at atmospheric pressure. The error in the calculated elastic properties, depending on the error in the determination of V_{l0} and v_{t0}, amounted to 1% in the case of the bulk moduli, 0.5% for Young's modulus, 0.9% for the shear modulus, 1.6% for Poisson's ratio, and 0.5% for the Debye temperature.

Using samples of different lengths, placed in a high-pressure chamber,[9] we determined at a given temperature, using an ultrasonic pulse method, the variation with pressure of the transit times of the longitudinal Δt_l (10 experiments) and transverse Δt_t (12 experiments) ultrasonic waves. At the same time, we determined the variation with pressure, Δl, in the length of a sample. We found that the pressure dependences of Δt_l, Δt_t, and Δl, obtained in each experiment, had a clear discontinuity both when the pressure was increased and reduced. The magnitude of the discontinuity was 2—3 times greater than the experimental error and indicated the presence of a phase transition. The observed phase transition exhibited hysteresis. For increasing pressure, the transition began at 18 000 kg/cm^2, while for decreasing pressure, it commenced at 17 000 kg/cm^2. We assumed the transition pressure to be 17 500 kg/cm^2.

The velocities of the longitudinal and transverse waves were determined as a function of pressure

$$v(p) = [l_0 - \Delta l(p)] \times [l_0 / v_0 - \Delta t(p)]^{-1}, \qquad (1)$$

where l_0 is the initial length of a sample and v_0 is the velocity of propagation of an ultrasonic

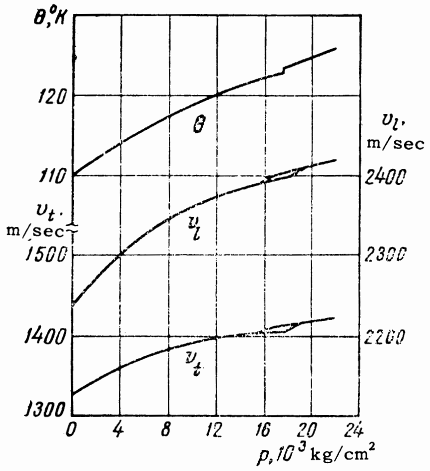

FIG. 1. Pressure dependence of the velocities of the longitudinal and transverse ultrasonic waves and of the Debye temperature of barium.

wave at atmospheric pressure. For each experiment, the values of the velocities fitted well a smooth curve; the scatter in the dependence $v_l(p)$ was 0.08%, and 0.12% for $v_t(p)$, while the magnitude of the discontinuity for $v_l(p)$ was 0.15% and for $v_t(p)$ was 0.48%. The pressure dependences of the longitudinal $v_l(p)$ and transverse $v_t(p)$ waves recorded in different experiments deviated by 0.2—0.3% from the average dependences.

Figure 1 shows the dependences $v_l(p)$ and $v_t(p)$ determined experimentally. When the pressure was increased, the two velocities rose nonlinearly, being ≈ 8% higher at 22 000 kg/cm².

The averaged-out functions $v_l(p)$ and $v_t(p)$ were used to determine the density of barium at high pressures using the formula

$$\rho(p)=\rho_0+(1+\Delta)\int_0^p\frac{dp}{v_l^2(p)-{}^4\!/_3 v_t^2(p)},$$

$$\Delta=\frac{9\alpha^2T}{c_pJ}\left(v_{l0}^2-\frac{4}{3}v_{t0}^2\right), \tag{2}$$

where $\alpha = 1.9 \times 10^{-5}$ deg^{-1}, $c_p = 6.870$ cal-g^{-1}-atom^{-1} deg^{-1}, T = 298°K. The density $\rho_0 = 3.607$ g/cm³ was determined from the atomic weight and from the lattice parameter of barium a = 5.019 Å. From the values of the density and from the elastic wave velocities, we determined the bulk moduli K_S and K_T, Young's modulus E, the shear modulus G, Poisson's ratio σ, and the Debye temperature Θ at pressures from 0 to 22 000 kg/cm².

Figure 2 shows the pressure dependences of the density of barium obtained by us, as well as the pressure dependences calculated from volume changes under pressure using the x-ray structure data [10] and the data obtained by the linear compressibility method. [3] The initial density was assumed to be 3.607 g/cm³. It is evident from Fig. 2 that our data are in good agreement with the results of earlier investigations. The relative change in the density at 22 000 kg/cm² was 21%.

The same figure (curve 1) shows the pressure dependence of the instantaneous compressibility, i.e., the reciprocal of the isothermal bulk modulus, obtained by the ultrasonic method. This dependence is nonlinear and is described satisfactorily by a quadratic polynomial up to p = 17 500 kg/cm²:

$$\varkappa=\frac{1}{K_T}=-\frac{1}{V}\frac{dV}{dp}$$

$$=103.13\cdot10^{-7}-2.4026\cdot10^{-10}p+5.073\cdot10^{-15}p^2 \tag{3}$$

(curve 1), determined by the least-squares method. From this polynomial, it is easy to determine the "normal" compressibility [11]

$$\varkappa_0=-\frac{1}{V_0}\frac{dV}{dp}=\frac{\rho_0}{\rho}\frac{1}{K_T} \tag{4}$$

(curve 2) and to compare it with the change in the "normal" compressibility under pressure found using the x-ray structure data

$$\varkappa_0=100\cdot10^{-7}-311.0\cdot10^{-12}\,p \tag{5}$$

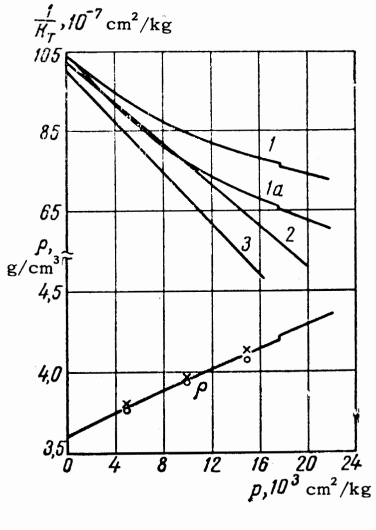

FIG. 2. Pressure dependences of the density and compressibility of barium, obtained by different methods. Instantaneous compressibility: curve 1, our data; normal compressibility; curve 1a – our data, 2 – Bridgman's data, 3 – Evdokimova and Vereshchagin's data. Density: continuous curve – our data, × – Bridgman's data, o – Evdokimova and Vereshchagin's data.

Elastic properties of barium up to the pressure of 22 000 kg/cm^2

	Pressure, kg/cm^2						Relative change	
	0	6000	12 000	17 500	20 000	22 000	at 22000 kg/cm^2	at transition
v_l, m/sec	2235	2323	2372	2397 2400	2410	2418	8.2±0.2	0.15
v_t, m/sec	1325	1374	1398	1407 1414	1420	1426	7.6±0.3	0.48
ρ, g/cm^3	3.607	3.822	4.024	4,202 4,219	4.300	4,361	20,9±0,3	0.47
E, 10^5 kg/cm^2	1.588	1,811	1,979	2.099 2,123	2.182	2,230	40,5±0,5	1.49
G, 10^5 kg/cm^2	0,646	0.736	0,802	0.848 0.860	0,884	0.904	40.0±0,8	1.73
K_S, 10^5 kg/cm^2	0,976	1.122	1.241	1.331 1,333	1.367	1,395	42.9±1.0	0,22
K_T, 10^5 kg/cm^2	0.965	1.107	1,222	1.309 1,311	1.344	1,371	42.2±1,0	0,21
σ	0.229	0.231	0.234	0.237 0,235	0.234	0.288	25,6±1.7	1.11
Θ, °K	109,9	116.0	120.0	122,6 123.3	124.7	125,8	14.5±0,6	0,63

(curve 3) and using the linear compression data:

$$\varkappa_0 = -\frac{1}{V_0}\frac{dV}{dp} = 101.87\cdot 10^{-7} - 254.84\cdot 10^{-12}p \qquad (6)$$

(curve 2).

As is evident from Fig. 2 and Eqs. (3), (5), (6), the values of the compressibilities obtained from measurements carried out by different methods are close but the nature of the change in the compressibility is different.

Figure 3 gives the pressure dependences of the adiabatic bulk modulus K_S, Young's modulus E, and the shear modulus G. As the pressure rises, the moduli increase nonlinearly and at 22 000 kg/cm^2 they will have changed by 40%. At the phase transition, Young's modulus increases by 1.49%, the shear modulus by 1.73%, but the bulk modulus remains practically unchanged, which is in agreement with the analysis of Bridgman's experimental data, carried out by Ryabinin.[12]

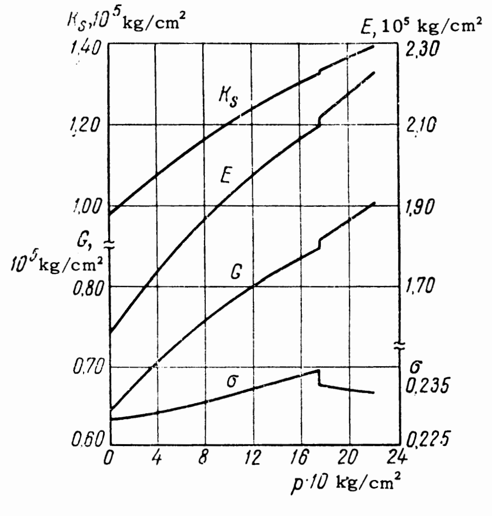

FIG. 3. Pressure dependences of the adiabatic bulk modulus, Young's modulus, the shear modulus and Poisson's ratio.

The Debye temperature (Fig. 1) is also a nonlinear ascending function of pressure and increases by 0.63% at the transition.

Poisson's ratio (Fig. 3) increases up to 17 500 kg/cm^2, decreases by 1.11% at the transition and continues to decrease slowly beyond the transition. It should be mentioned that the probable errors in the measurements of the velocities of ultrasound after the transition make it impossible to determine reliably the changes in Poisson's ratio above 17 500 kg/cm^2.

The absolute values of the elastic properties of barium at various pressures and their relative changes up to 22 000 kg/cm^2 are listed in the table, which also gives the errors in the relative changes in the elastic properties, governed by the deviation from the average dependences $v_l(p)$ and $v_t(p)$. The values of the discontinuities at the phase transition are also included.

Thus, we determined, by an ultrasonic pulse method, the pressure dependences of the longitudinal and transverse wave velocities, the bulk moduli, Young's modulus, the shear modulus, Poisson's ratio, and the Debye temperature of barium up to 22 000 kg/cm^2. A considerable increase in and nonlinearity of the properties were observed. The nonlinearity of the pressure dependences of the elastic properties of barium in the investigated range of pressures requires the use of elastic constants of orders higher than the third in the description of the behavior of this substance within the framework of the theory of finite deformations. Third-order elastic constants are probably also insufficient to describe the processes of deformation of less compressible substances over a wider range of pressures.

The ultrasonic method established a density discontinuity $\Delta\rho/\rho_0 = 0.47\%$ at the investigated phase transition at 17 500 kg/cm^2, which is in agreement with the value of 0.6% determined by Bridgman. Since the x-ray structure investigations [6] have shown that up to 59 kbar barium has a body-centered cubic lattice, which transforms at 59 kbar into a close-packed hexagonal lattice type A, the 17 500 kg/cm^2 transition is obviously isomorphous. The ultrasonic data on barium do not make it possible to determine unambiguously the nature of this transition and additional investigations, using various methods, are required to establish whether the phase transition involves some rearrangement of the crystal lattice or perhaps transition of one of the two 6s-electrons to the 5d-level. According to Alekseev's calculations [13], an electron transition takes place when the interatomic spacings in barium are reduced by 10%. According to our measurements, the interatomic spacings decreased by ≈6% at 17 500 kg/cm^2.

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