Pressure and temperature dependences of acoustic-wave velocities in polycrystalline bismuth*

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Ultrasonic velocity measurements have been made on polycrystalline bismuth as a function of temperature and pressure over the temperature and pressure ranges 23–160 °C (at atmospheric pressure) and 0–28.4 kbar (at 23 °C), respectively. Special care was taken with the room-temperature and pressure measurements in an attempt to resolve discrepancies in previously reported sound velocity measurements. The data have been used to determine the pressure-temperature dependences of various elastic parameters, including the (discontinuous) changes across the I-II and II-III phase boundaries. The pressure data are the first that have been taken under truly hydrostatic conditions, and they are compared to results obtained with solid pressure transmitting media.

I. INTRODUCTION

Bismuth has been a material of great interest in the area of high-temperature high-pressure physics ever since the pioneering work of Bridgman.[1] This early work showed bismuth to have a number of interesting features, including a melting temperature that is initially a decreasing function of pressure, and a number of pressure-induced solid-state transitions. Two of these transitions occur at fairly low pressures (I-II at 25.4 kbar and II-III at 26.8 kbar) and are characterized by sharp volume and resistivity discontinuities.[2]

In recent years there have been a number of experimental studies of shock-wave propagation in bismuth.[3-6] One question of special interest in this area is whether melting (or partial melting) can occur on the time scale involved in a shock-wave experiment. Bismuth is an ideal material for studying possible shock-induced melting, because it has a relatively low melting temperature which decreases with increasing pressure. Early experimental work along these lines[3] suggested that melting does not occur on the microsecond time scale of shock experiments, but rather that bismuth remains in a metastable solid state when shocked to temperatures and pressures above the equilibrium melting boundary. In fact, this work suggested that a solid-state phase transition corresponding to the metastable extension of the I-II phase boundary was observed. More recent shock-wave studies[6] employing instrumentation of much higher resolution and samples with a finer-grain structure have indicated that it is very likely that at least partial melting can occur under shock-loading conditions.

In order to interpret the observed shock-wave profiles, it is advantageous to be able to predict from theoretical models what profiles should be expected for the two cases of melting (or partial melting) and nonmelting. In order to do this, it is necessary to have a characterization of the physical properties of the three phases involved (solid I, solid II, and liquid). Measurements of acoustic-wave propagation in these various phases can provide information that is useful in two ways. A knowledge of the pressure and temperature dependences of the acoustic velocities can be utilized in determining the equation-of-state surfaces of the phases, thereby providing input information for hydrodynamic model calculations of shock-wave profiles. Acoustic velocity data can be further utilized to aid in determining the shock response for models incorporating elastic response.

These considerations were our primary motivation for making measurements of the pressure and temperature dependences of acoustic-wave velocities in bismuth. A further motivation was to attempt to gain some information concerning the solid-state transitions I-II and II-III. There have been several recent acoustic investigations of these transitions,[7-9] and these investigations showed a large (~25%) decrease in the shear-mode velocity in phase II relative to phases I and III, as well as a large relative acoustic attenuation in phase II. However, these previous measurements were not consistent with regard to either the values of the velocities at atmospheric pressure or the magnitudes of the discontinuities at the two high-pressure phase transitions. Furthermore, none of these measurements were made under truly hydrostatic pressure conditions, and it is possible that the presence of shear stresses could adversely affect the measured pressure dependences. It was therefore felt that careful measurements under hydrostatic pressure conditions could resolve the above-mentioned inconsistencies.

We have made two sets of acoustic measurement on samples of fine-grained (~30 μ) polycrystalline bismuth. First, we have measured the longitudinal and shear velocities as a function of hydrostatic pressure up to 28.4 kbar at room temperature. Second, we have measured these velocities as a function of temperature in the range 23–160 °C. The experimental details of this work will be described in Sec. II and the data analysis procedures in Sec. III. Results will be presented for the pressure and temperature dependences of the longitudinal and shear sound velocities and for various elastic parameters that can be deduced from these velocities. In Sec. IV our results will be discussed and compared to the earlier acoustic studies. The main emphasis of Sec. IV will be on the discussion of what can be deduced concerning the nature of the high-pressure phase transitions. Detailed discussions of the equation of state of bismuth will appear elsewhere.[6]

II. EXPERIMENTAL

The samples used were prepared from bismuth powder which was 99.999% pure with respect to metallic impurities. The powder was isostatically pressed[10] into a disk at 60 000 psi and 150 °C. Subsequently, the sample disk was annealed in an argon atmosphere at 240 °C for

6 h. The samples used for the experimental runs were all cut from the same disk. They were about 0.4 cm thick and had cross-sectional dimensions of about 0.7 cm. The density was measured to be 9.728 g/cm², about 99.3% of the single-crystal value. This departure from theoretical density is believed to be due to small amounts of oxide impurities. The average grain size, as determined by a metallographic technique, was about 30 μ.

Two ultrasonic techniques were used for the acoustic velocity measurements. The pulse-echo technique was used for most of the high-pressure runs. The pulse superposition technique[11] was used for the temperature runs and for some of the pressure runs.

Special care was taken in measuring the longitudinal and shear wave velocities at room temperature and atmospheric pressure. These measurements were made with both of the above-mentioned ultrasonic techniques. They were made at two frequencies, 2 and 5 MHz, and they were checked with different bonding materials (Dow resin V-9, phthalic anhydride-glycerin polymer, and Nonaq stopcock grease) and with samples of different thickness. The major problem encountered in these velocity measurements was the correct identification of the corresponding rf cycles in the successive echoes. This identification is difficult because of attenuation in the samples, and we believe that this difficulty has led to errors in the sound velocities previously reported in the literature. We believe that we were able to unambiguously determine the correct corresponding cycles using the above-mentioned procedure.

The measurements as a function of pressure were made with the sample in a standard Bridgman press utilizing a 50-50 mixture of pentane and isopentane as the hydrostatic pressure medium. Pressure was measured by a calibrated manganin coil inside the pressure chamber. The ultrasonic transducers were bonded directly to the sample with a phthalic anhydride-glycerin polymer. This polymer was made by heating a mixture of the two constituents to about 150 °C for 5–10 min. A fairly nonviscous preparation was used. The large differential compression between the sample and the quartz transducers, combined with the increased stiffness of the bond at high pressure, often caused the transducers to break during the high-pressure runs. This breakage usually did not occur, however, if small-diameter transducers were used. It was found that transducers $\frac{1}{8}$ in. in diameter could be used at 5 MHz and transducers $\frac{1}{4}$ in. in diameter at 2 MHz.

The measurements of the changes in ultrasonic transit time as a function of pressure were relatively straightforward, with the only difficulty being tracking the transit times as the sample went through the two high-pressure phase transitions. Although the attenuation was large as the sample was transforming, it was possible to observe two echoes and track the transit times continuously during the transformations. Most of the runs were done at 5 MHz, with 2-MHz runs being made to verify the large changes at the phase transitions. The agreement in the velocity changes observed across the phase boundaries at these two frequencies indicates that the correct changes were observed in the above-mentioned tracking procedure. Although we did not measure the ultrasonic attenuation, we found it to have qualitatively the same pressure dependence as shown by Heydemann.[8] Especially remarkable was the fact that the attenuation was very low in phase III, and up to 10 or 12 echoes could be seen. When the pressure was lowered from phase III to II, the attenuation became so large as to prohibit data to be taken with decreasing pressure.

For the measurements as a function of temperature, the sample was mounted in a brass holder which fitted inside a temperature-controlled tube furnace. Data were taken only when the temperature was changing at a rate of less than 0.5 °C/min. Temperature was measured with a chromel-alumel thermocouple affixed to the sample. Two bonding materials were used for the transducers, Epon epoxy and waterglass cement, and gave consistent results. Data will be reported here for the temperature range 23–160 °C. For the temperature runs, the pulse superposition technique at a frequency of 5 MHz was used.

The data for the pressure runs are shown in Fig. 1, which is a plot of the reduced transit time for each mode (longitudinal and shear) as a function of pressure. In Fig. 1 solid plotting symbols represent stable points—values of $t(p)$ which were not changing in time—and open plotting symbols represent points obtained while the sample was actually in the process of transforming from one phase to another. The solid lines in Fig. 1 are

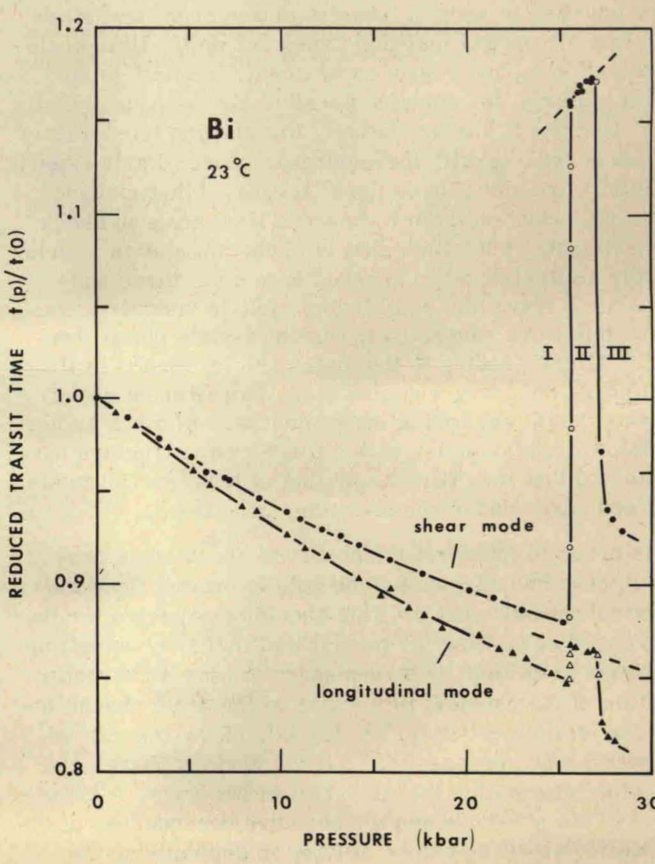

FIG. 1. Reduced ultrasonic transit time vs pressure data. Open plotting symbols represent unstable points taken while sample was transforming. Solid plotting symbols represent stable points.

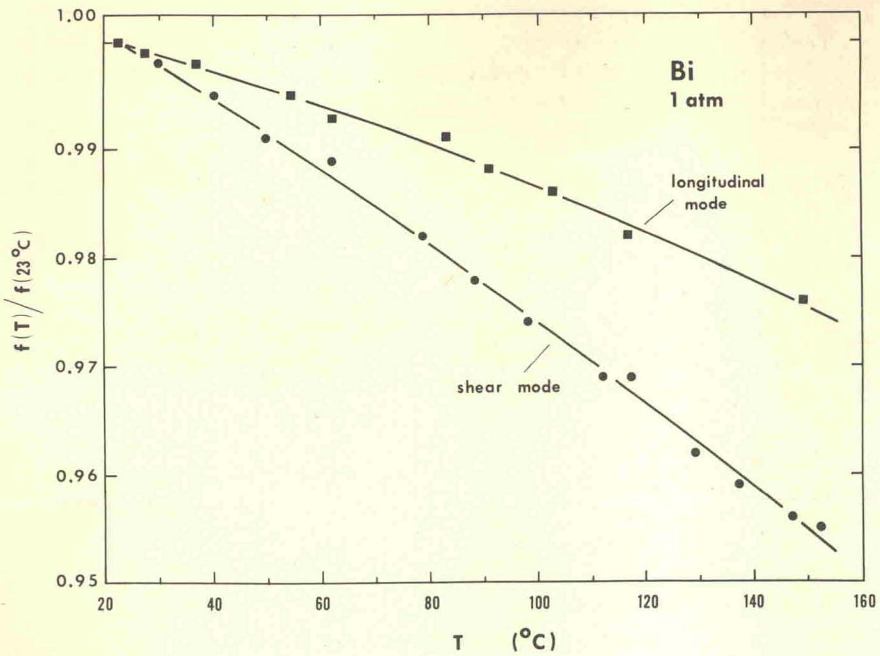

FIG. 2. Reduced repetition rate data as a function of temperature.

smooth curves that were drawn by eye through the data points. These smooth curves were used for the data analysis to be discussed in Sec. III. The dashed lines are straight lines representing the transit times in phase II. There are several interesting features of the transit-time data that may be noted. The most striking feature is the large increase in the shear-mode transition time in phase II, which corresponds to a decrease in the velocity. The shear velocity is a decreasing function of pressure in phase II. The changes in the longitudinal mode across the phase boundaries are much smaller than for the shear mode, and the longitudinal-mode velocity increases normally with increasing pressure in all three phases. These features are qualitatively the same as those noted in previous work.[7-9] One feature not previously reported is the large amount of curvature in the transit-time data in phase III. The work of Refs. 7 and 9 indicate nearly linear behavior of the transit times as a function of pressure in this phase. Special care was taken to establish that this curvature is real. Stable transit-time values were obtained within ~15 min after a change of pressure, and these stable values were held for times of up to 30 min for some of the points in the curved region.

The temperature data are shown in Fig. 2. Since all the temperature data were obtained by the pulse superposition technique, we have represented the data by the reduced repetition rate ratio $f(T)/f(23\,°\mathrm{C})$. Here f is the inverse of the transit time, $f=t^{-1}$. The relatively large amount of scatter is due to less than ideal ultrasonic bonding between the transducer and sample. These data indicate normal decreases of the acoustic velocities with increasing temperature, and are qualitatively in agreement with what one would expect based on high-temperature measurements of the single-crystal elastic constants of bismuth.[12]

III. DATA ANALYSIS

In order to determine the ultrasonic velocities as a function of pressure and temperature from the transit-time data represented in Figs. 1 and 2, it is necessary to know the changes in the acoustic path length as the pressure or temperature is varied. The temperature correction is small because of the relatively low thermal expansion of bismuth. We used the value[13] $\alpha = 4.2\times10^{-5}/°\mathrm{C}$ for the volume thermal expansion coefficient, and we assumed α to be constant over our temperature range.

The determination of the path length changes as a function of pressure requires somewhat more care because of the relatively large compressibility of bismuth and the discontinuous volume changes at the I-II and II-III phase boundaries. A number of measurements have been made of the compression of bismuth at high pressure,[1,2,9,14] and these experiments have not given consistent results, especially with regard to the discontinuities at the phase boundaries. For the I-II transition, values of $\Delta V/V_0$ ranging from 3.5 to 5.8% have been given, and for the II-III transition the range is 2.7 to 3.6%. We have used the compression data of Giardini and Samara[14] for reducing our data. These authors measured the compression with a sensitive and accurate inductive coil technique, whereas the other compression measurements were made by the piston-cylinder displacement technique. Dr. Samara has kindly made his original compression data available to us.

The pressure and temperature dependences of the acoustic velocities were determined as described above from the smooth curves of Figs. 1 and 2. The high-pressure results are shown in Fig. 3 and the temperature results are tabulated in Table I. For numerical reference, the pressure data are partially tabulated in Table II. From the acoustic data, it is possible to deduce various elastic properties of bismuth as a function of pressure and temperature. In Fig. 4 we have plotted the longitudinal, shear, and bulk moduli (L, μ, and B, respectively) and Lamé's λ, as a function of pressure. These results are also partially tabulated in Table II,

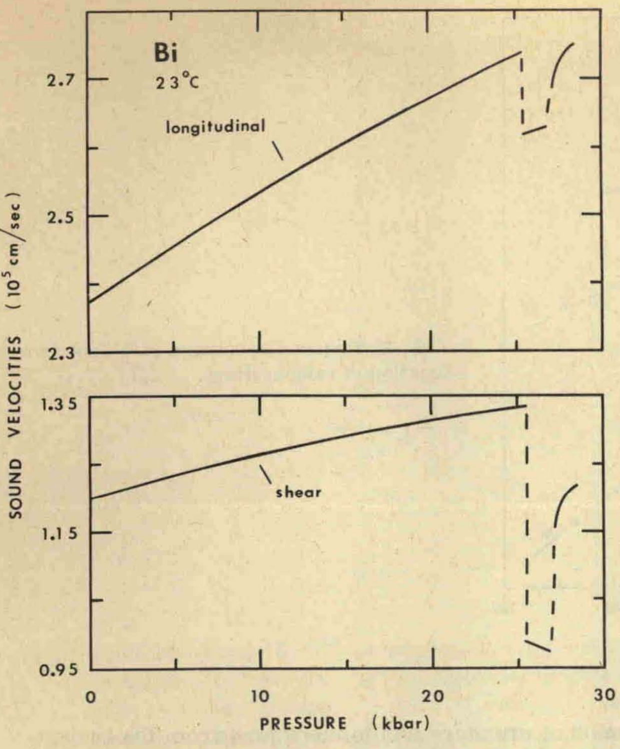

FIG. 3. Longitudinal and shear velocities as a function of pressure.

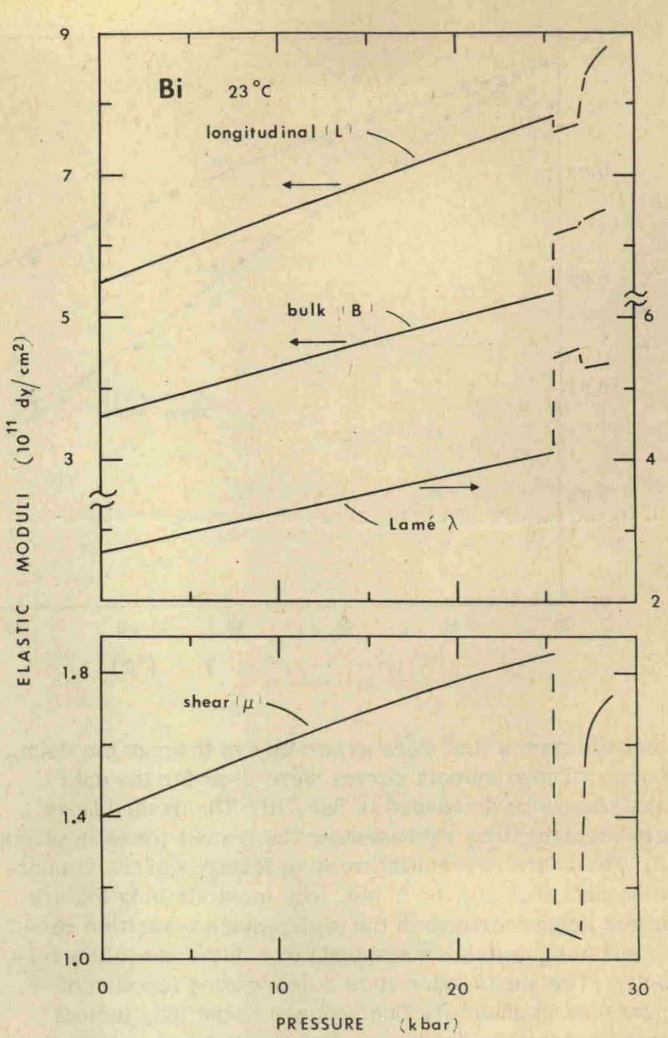

FIG. 4. Pressure dependences of various elastic moduli.

along with the Young's modulus Y and Poisson's ratio σ. The temperature dependences of the various elastic moduli are also tabulated in Table I. All values quoted for the moduli are adiabatic values. The number of significant digits retained in Tables I and II are not meant to reflect either the accuracy or the precision of the results. The over-all accuracy of the results is about 1% for the velocities and 2% for the moduli.

In Table III we have listed the temperature derivatives of the velocities and other elastic parameters at 23 and 160 °C. The Lamé λ was nearly constant with temperature and the value listed in Table III was approximated from a straight line through the whole temperature range. Pressure derivatives taken from Figs. 3 and 4 for phases I and II are listed in Table IV. The entries in Tables III and IV are considered accurate to about 7%.

IV. DISCUSSION AND CONCLUSION

The present data have been used by Johnson *et al.*[6] to help define the equation of state of Bi II. These authors used a constant value of $B = 615$ kbar for phase II, and, in the absence of specific heat data, they assumed that C_V has the Dulong-Petite value of $3R$. Reference 6 may be consulted for further details of the equation-of-state determination and for details of stress-wave calculations

TABLE I. Temperature dependences of various elastic properties of polycrystalline bismuth as calculated from smooth curves of Fig. 2. The quantities tabulated are longitudinal velocity v_l; shear velocity v_t; longitudinal modulus L; shear modulus μ; Lamé λ; Young's modulus Y; and Poisson's ration σ.

T (°C)	v_l (10^5 cm/sec)	v_t (10^5 cm/sec)	L (10^{10} dyn/cm^2)	μ (10^{10} dyn/cm^2)	λ (10^{10} dyn/cm^2)	Y (10^{10} dyn/cm^2)	B (10^{10} dyn/cm^2)	σ
20	2.376	1.201	54.93	14.04	26.85	37.30	36.21	0.3283
40	2.369	1.194	54.57	13.86	26.85	36.86	36.09	0.3297
60	2.362	1.186	54.21	13.67	26.85	36.40	35.96	0.3314
80	2.354	1.178	53.78	13.48	26.82	35.93	35.81	0.3327
100	2.346	1.170	53.34	13.28	26.78	35.44	35.63	0.3343
120	2.336	1.162	52.88	13.07	26.74	34.92	35.45	0.3358
140	2.326	1.152	52.37	12.86	26.65	34.39	35.22	0.3373
160	2.315	1.143	51.83	12.64	26.55	33.84	34.98	0.3387

TABLE II. Pressure dependences of various elastic properties of polycrystalline bismuth at $T=23\,^{\circ}\mathrm{C}$ as calculated from smooth curves of Fig. 1.

P (kbar)	Phase	v_l (10^5 cm/sec)	v_t (10^5 cm/sec)	L (10^{10} dyn/cm^2)	μ (10^{10} dyn/cm^2)	λ (10^{10} dyn/cm^2)	B (10^{10} dyn/cm^2)	Y (10^{10} dyn/cm^2)	σ
0	I	2.375	1.200	54.87	14.01	26.85	36.19	37.23	0.329
25.4	I	2.738	1.334	77.94	18.50	40.94	53.27	49.74	0.344
25.4	II	2.618	0.990	76.01	10.87	54.27	61.52	30.80	0.417
26.8	II	2.629	0.977	76.89	10.62	55.65	62.73	30.16	0.420
28.4	III	2.748	1.217	88.0	17.26	53.48	64.99	47.57	0.378

for the shock-melting experiments. The rest of the present discussion will be concerned with the comparison of our high-pressure data with previous high-pressure measurements and a discussion of several factors pertinent to the nature of the high-pressure phases.

The first reported acoustic measurements on bismuth through the I-II and II-III transitions were made by Matsushima.[7] These measurements were made with talc as the pressure transmitting medium and with $BaTiO_3$ transducers directly affixed to the sample. There were two difficulties associated with this experiment. First, the transit-time data exhibited a large scatter (especially for the longitudinal mode) which limited the precision of the data. A more serious problem is that the compression of the sample was not known accurately due to the fact that this compression was estimated from the high-pressure piston displacement, and it was, therefore, necessary to take into account the compression of the talc. Despite these difficulties, Matsushima's results are in reasonably good qualitative agreement with ours. His 1 atm velocities are $v_l=2.22\times10^5$ cm/sec and $v_t=1.20\times10^5$ cm/sec, the former being about 7% lower than our value and the latter agreeing exactly. Our relative shear and longitudinal velocity changes up to the I-II boundary are a few percent smaller than Matsushima's values. The changes across the I-II and II-III transitions agree reasonably well for the longitudinal mode. For the shear mode, Matsushima found a 34% velocity discontinuity at the I-II transition as compared to our jump of 26%.

Heydemann[8] has given a brief account of measurements of longitudinal wave transit time and attenuation in polycrystalline bismuth obtained in a piston cylinder apparatus with the ultrasonic transducers affixed to the high-pressure piston. As mentioned above, our qualitative observation of the attenuation agrees with this work. Heydemann observed changes in the longitudinal velocity with time which he attributed to "recrystallization" of the sample. This recrystallization was reported to take place with the sample held at 16 kbar. We never observed any such recrystallization effects in our runs except for possible recrystallization across the II-III phase boundary. Our longitudinal velocity data seem consistent with the results obtained by Heydemann after the reported recrystallization of his sample.

Recently, Voronov and Stal'gorova[9] (VS) have reported measurements of the bismuth longitudinal and shear velocities, again using a piston cylinder apparatus with transducers external to the pressure cell. The changes in sound velocities as a function of pressure reported by VS are in good agreement with our results, indicating that shear stress effects in their apparatus were not excessive. Our major disagreement with these authors is on the values of the atmospheric-pressure velocities; the values of VS are $v_l=2.229\times10^5$ cm/sec and $v_t=1.114\times10^5$ cm/sec.

Our high-pressure results show some interesting features pertaining to the polymorphic I-II and II-III transitions. The most interesting feature is undoubtedly the dramatic changes of the shear velocity across the phase boundaries. Of further interest is the fact that the shear velocity is a decreasing function of pressure within phase II. These observations suggest the existence in Bi II of one or more acoustic phonon modes with anomalously low velocities and negative pressure derivatives dv/dp. A correlation between low (or negative) values of $d\mu/dp$ and both low values of μ/B and large values of σ has been noted for a number of polycrystalline oxides by Anderson.[15] The properties of Bi II are in line with the general trend of these oxides. It has also been noted[16] that crystals having shear modes with negative pressure dependences generally undergo pressure-induced polymorphic transitions, and the negative value of $d\mu/dp$ in phase II may be considered another manifestation of this phenomenon.

The acoustic behavior in phase III is also interesting.

TABLE III. Temperature derivatives of various elastic properties of polycrystalline bismuth measured at atmospheric pressure. All are in units of $10^{-4}\,{}^{\circ}\mathrm{C}^{-1}$.

T (°C)	$\frac{d\ln v_l}{dT}$	$\frac{d\ln v_t}{dT}$	$\frac{d\ln L}{dT}$	$\frac{d\ln \mu}{dT}$	$\frac{d\ln \lambda}{dT}$	$\frac{d\ln Y}{dT}$	$\frac{d\ln B}{dT}$	$\frac{d\sigma}{dT}$
23	−1.7	−3.0	−3.3	−6.4	−0.6[a]	−6.0	−1.7	0.74
160	−2.6	−4.2	−5.3	−8.7		−8.2	−3.4	0.74

[a]Average slope 20–160 °C (see text).

TABLE IV. Pressure derivatives of various elastic properties of polycrystalline bismuth measured at room temperature. All are in units of 10^{-3} kbar^{-1}.

P (kbar)	Phase	$\frac{d \ln v_l}{dp}$	$\frac{d \ln v_t}{dp}$	$\frac{d \ln L}{dp}$	$\frac{d \ln \mu}{dp}$	$\frac{d \ln \lambda}{dp}$	$\frac{d \ln B}{dp}$
0	I	6.7	5.6	16.9	14.5	19.4	18.1
25.4	I	4.5	2.7	10.9	7.5	13.8	12.5
25.4	II	3.0	−9.4	8.3	−16.4	18.2	14.0

The curvature of the data for this phase indicate a progressive softening of the lattice as pressure is decreased toward the III-II boundary. Although the II-III transition is of first order, the volume anomaly is quite small and the transition may be near enough to being of second order that (incipient) thermodynamic anomalies might be observable. The data suggest that there might possibly be an incipient soft acoustic mode for the III-II transition. Unfortunately, the structure of Bi III has not been unambiguously determined so that it is not as yet possible to predict what acoustic modes, if any, could be anomalous. Measurements of sound velocities in single crystals at high pressure might well be useful for further clarification of the detailed nature of the high-pressure transitions.

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