TABLE II. Pressure dependences of various elastic properties of polycrystalline bismuth at $T = 23\,°C$ 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 $10^{-4}\,°C^{-1}$.

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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