

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

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(Received 9 August 1973)

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.

SEP 4 1974

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 lines³ 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 studies⁶ 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 pressed¹⁰ 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/cm³, 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 technique¹¹ 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 non-viscous 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

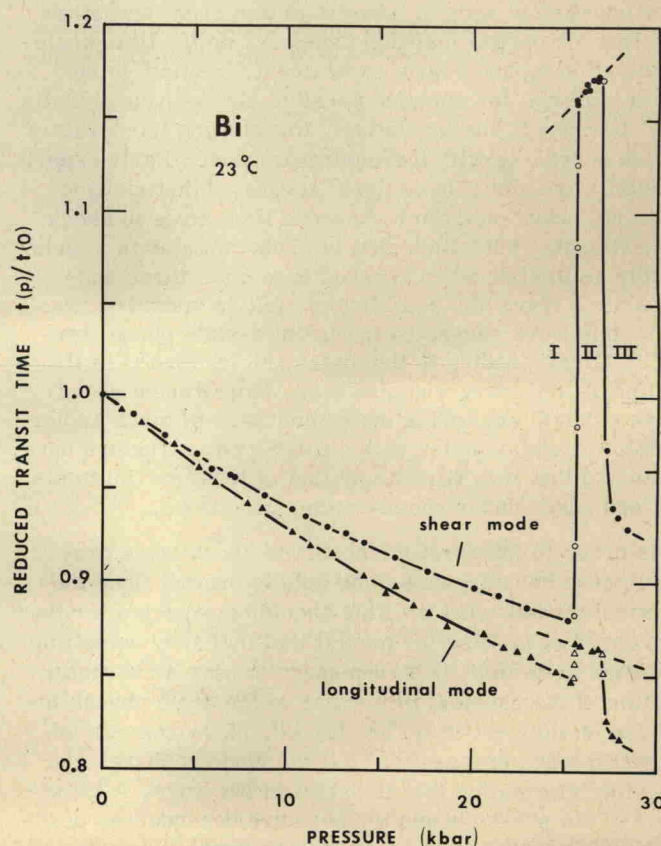


FIG. 1. Reduced ultrasonic transit time vs pressure data. Open plotting symbols represent unstable points taken while sample was transforming. Solid plotting symbols represent stable points.