## COMPRESSIBILITY OF BISMUTH AND ITS UPPER TRANSITION PRESSURE 1525

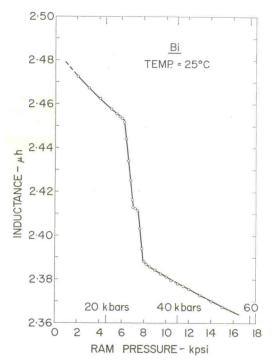


FIG. 1. Inductance of a coil wound on a threaded Bi core as a function of ram pressure at room temperature. Lead inductance was  $0.5800 \ \mu\text{H}$ .

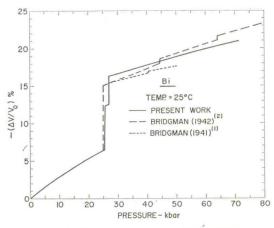


FIG. 2. Compression curve of Bi at 25°C.

The compression curve of Bi to 60 kbar at 25°C is shown in Fig. 2 which also shows Bridgman's results for comparison. The data is tabulated at 5 kbar increments in Table 1. These results are

Table 1. Compression of Bismuth at 25°C.\* The listed values are the means and standard deviations for eight experiments

P (kbars)	$-(\Delta V/V_0)$ %	P (kbars)	$-(\Delta V/V_0)$ %
0	0	35	$17 \cdot 2 + 0 \cdot 8$
5	1.5	40	$17.8 \pm 0.9$
10	2.8	45	$18.3 \pm 0.9$
15	4.1	50	$18.9 \pm 0.9$
20	5.3	55	$19.4 \pm 1.0$
25	6.3	60	$19.9 \pm 1.0$
30	$16.7 \pm 0.8$		

\* Matched with BRIDGMAN's<sup>(2)</sup> data up to 20 kbar.

† (i) Transition at 25.4 kbar; compressions -6.4% to  $-(12.2\pm0.4)\%$ ; (ii) Transition at 26.8 kbar; compressions  $-(12.4\pm0.5)\%$  to  $-(16.0\pm0.8)\%$ .

based on eight runs for which the experimental set-ups differed among each other in some respect, such as sample size, pressed powder vs. cast samples, thickness of silver chloride jacket (when used), and whether or not a thin pyrophyllite sleeve was placed on the coil before enclosing it in silver chloride. On completely identical set-ups the reproducibility was better than  $\pm 2\%$  of the vol. changes themselves.

The over-all results are in fairly good agreement with Bridgman's data. The most significant differences occur in the region of the transitions. The Bi<sub>I-II</sub> and Bi<sub>II-III</sub> transitions occur so close together in pressure that it was beyond the resolving powers of Bridgman's 50 kbar<sup>(1)</sup> and 100 kbar<sup>(2)</sup> apparatus to separate them. In earlier lower pressure work, however, he reported the vol. changes at the two transitions separately.<sup>(9)</sup> Table 2 compares the results and also includes LAMORI's<sup>(10)</sup> data obtained by the piston displacement technique.

The ratios of the sudden vol. changes I-II: II-III varied between 1·41:1·0 and 1·60:1·0 for the various runs. By way of comparison BRIDG-MAN's data<sup>(9)</sup> yielded a ratio of 1·53:1·0 and that of LaMori 1·33:1·0. It is not clear why there should be such a large scatter in this ratio. In his resistance work, BRIDGMAN<sup>(3)</sup> also observed a wide variation in the ratio of the resistance changes Table 2. Vol. changes for the Bi<sub>I-II</sub> and Bi<sub>II-III</sub> transitions at 25°C. The atmospheric vol. is taken as the reference vol. in calculating the per cent vol. changes

	$-(\Delta V/V_0)\%$ I-II	$-(\Delta V/V_0)\%$ II-III	$-(\Delta V/V_0)\%$ I-II-III
Present work	5-8	3.6	9.6
BRIDGMAN <sup>(2)</sup>			8.6
BRIDGMAN <sup>(9)</sup>	4.6	3.0	
LAMORI <sup>(10)</sup>	4.8	3.6	9.0

at the two transitions. It is unfortunate that the structure of phase II is still not known, for that might help to clarify this point.

The total compression of Bi II is  $(0.23 \pm 0.10)$ %. The accuracy here is not too great since this value represents the difference between two large and nearly equal numbers.

There was no evidence in any of the experiments on either the up- or down-pressure cycles of the transition observed by Bridgman at ~44 kbar. Similarly, many attempts up to 70 kbar failed to show any indication of a transition at  $\sim 64$  kbar. The reported vol. changes for these two transitions are 0.6% and 0.5%, respectively. The inductive coil technique has been demonstrated capable of quantitatively detecting sudden vol. changes of < 0.1%.<sup>(5)</sup> Thus, the transitions in question should have been clearly exhibited by the data. It might be mentioned here that a cursory study was made on the possible influence of selected contaminants in trace amounts of activating these transitions. Respective contaminants of Li, Mn, Ni, Zn, Ge, Sn, Sb, Te, Ir, Hg, Pb, Pr, Sm, Tb, and Yb in concentrations of approximately 1 at.% were investigated. All proved ineffective in bringing out the transitions.

One experiment was made at 170°C, and the results are shown in Fig. 3. The I–II transformation occurs at 18 kbar in agreement with BRIDGMAN's<sup>(9)</sup> observations. The sudden vol. changes at the transitions are  $6\cdot1\%$  for I–II and  $3\cdot9\%$  for II–III.\* At 170°C Bi II has a stability range from 18 to 23 kbar. Its compression over this range is  $1\cdot00\%$ .

Finally, it should be pointed out that no corrections were applied to the present data other than subtracting the inductance of the leads from the total measured inductance. This was a constant for each experiment and varied between 8% and 50% of the total inductance for the various runs. The principal source of error in the technique is the change in inductance caused by distortion of the coil and leads.<sup>(6)</sup> This contribution is well within the scatter of the data.

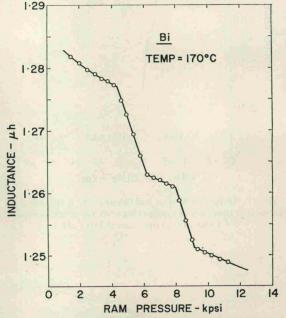


FIG. 3. Inductance of a coil wound on a threaded Bi core as a function of ram pressure at 170°C. Lead inductance was  $0.6630 \mu$ H.

The resolution of the inductive coil technique, particularly in separating the first two transitions in Bi, is much superior to the piston displacement method, In over fifty runs, we never failed to see the sharp step separating the two transitions (see Figs. 1 and 3).

## The Upper Bi Transition

At present, the highest reasonably well established "fixed" point used in pressure calibration is the 59 kbar Ba transition which is generally believed to be accurate to  $\pm 3\%$ . The next higher widely used "fixed" point is the upper Bi transition long believed to be at 88 kbar. On the basis

<sup>\*</sup> Based on the atmospheric vol. as reference.