I-II Transition

Pressurization Procedure	$P_{I\text{-}II}$, K-atm	$P_{II\text{-}I}$, K-atm	$\Delta P_{I\text{-}II}$, K-atm
500-atm increments	24.23 (24.10-24.50)	23.29 (22.90-23.50)	0.94 (0.60-1.20)
250-atm increments	24.25 (24.20-24.30)	23.20 (23.00-23.50)	1.05 (0.75-1.30)
100-atm increments	24.20 (24.05-24.30)	23.49 (23.40 23.70)	0.71 (0.55-0.90)
Uninterrupted at 50 atm per min.	24.31 (24.25-24.35)	23.20 (23.15-23.40)	1.11 (0.95-1.20)

II-III Transition

Pressurization Procedure	$P_{II\text{-}III}$, K-atm	$P_{III\text{-}II}$, K-atm	$\Delta P_{II\text{-}III}$, K-atm
500-atm increments	25.55 (25.50-25.60)	24.84 (24.70-25.10)	0.71 (0.50-0.80)
250-atm increments	25.65 (25.60-25.70)	24.98 (24.95-25.00)	0.67 (0.65-0.70)
100-atm increments	25.70 25.70	25.15 (24.95-25.30)	0.55 (0.40-0.75)
Uninterrupted at 50 atm per min	25.75 25.75	25.13 (25.10-25.15)	0.62 (0.60-0.65)

the first cycle in case of recycling) in the specific category and the double values, in parentheses, the data spread. Although the differences are relatively small, it can be seen that the magnitude of the hysteresis in the I-II transitions tends to increase with increasing pressurization rates, which most probably is due to nonequilibrium conditions resulting in "over-driving" of the transitions.

Recycling several times through either of the transitions seems to have little, if any, effect on the magnitude of the hysteresis. For example, passing through the I-II transitions three times does not result in any consistent change in the hysteresis. Recycling four times through the II-III transition resulted in a reduction from 750 to 500 atm.

It is of concern whether the observed hysteresis is, in fact, a real phenomenon associated with these transitions or simply a function of the experiment. From the standpoint of the experiment, the two possible causes of observed hysteresis are substantial nonequilibrium associated with too rapid a pressurization rate and/or natural hysteresis in the manganin-coil pressure transducer.

Considering the first possibility, using 100-atm increments with a 5-min stabilization period there was usually a substantial period of elapsed time at the transition pressure before the transformation initiated. This is clearly shown in Fig. 3 which is a typical plot of relative resistance vs time as obtained from the continuous oscillographic recording of voltage change for simultaneously pressurized single and polycrystalline samples. Time = 0 on the abscissa corresponds to the time at which the transition pressure was reached. In any given experiment, the transitions normally did not initiate simultaneously in both samples. However,

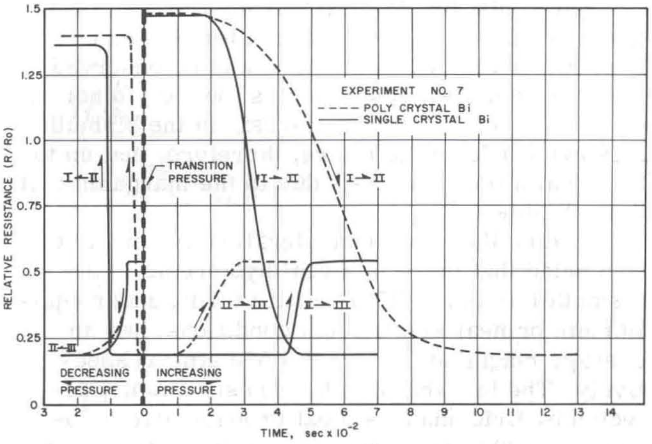

Fig. 3—Typical relative resistance vs time curves for I-II and II-III transitions.

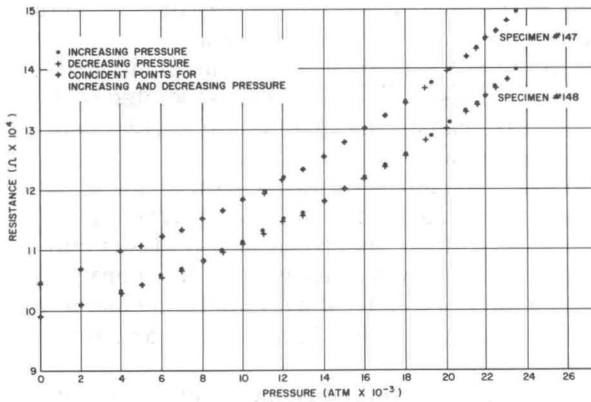

Fig. 4—Resistance vs pressure for single crystals.

considering the curve for the single crystal shown in Fig. 3 as an example, approximately 3 min elapsed before the I-II transition initiated and 7 min before the initiation of the II-III. For decreasing pressure, the elapsed time was approximately 1 and 2 min, respectively, for the III-II and II-I. Apparently, then, using 100-atm increments with a stabilization period is close enough to equilibrium conditions so that the hysteresis is not attributable to "overdriving" of the transitions. Using the larger pressure increments, the transitions often occurred during the increase or decrease of pressure, resulting in little or no elapsed time at the transition pressure and short durations of transformations. In these instances, there is a greater tendency to "overdrive" the transitions, resulting in an increase in the magnitude of the hysteresis.

That the observed hysteresis is not due to the manganin-coil transducer is based on the following two considerations. First, any hysteresis occurring in the pressure measurement would vanish at the peak pressure and be a maximum at the midpressure range. However, the hysteresis in the transition was observed even when the applied pressure just exceeded the transition pressure by a few hundred atmospheres, and also in the case of the partial I-II transformation. Second, as a further check, two bismuth single crystals were pressurized to just below the I-II transition. The relative resistance vs pressure data for this experiment is shown in Fig. 4. Since there was no observed structure change in the samples, one would not expect to see any natural hysteresis in the bismuth. It is evident from the figure, therefore, that up to 23,500 atm the hysteresis due to the manganin coil is negligible.

Based on the above considerations, it must be concluded that there is a real hysteresis in the bismuth I-II and II-III transitions that, under equilibrium or near equilibrium conditions, has an average magnitude of 730 and 550 atm, respectively. The fact that this hysteresis was not detected by Bridgman[1] is most probably due to his utilizing 1000-atm increments in the region of the transition. Since the pressure increments used in his research were approximately the same size as the hysteresis observed in this work, it could have readily gone without detection.

B) Relative Resistance. Some mention should be made of the resistance changes associated with the bismuth transitions, particularly with respect to their structural implications.

Relative resistance (R_p/R_0) data at the transition pressure from all experiments are summarized as follows according to initial structure, where the single value represents the average from all experiments (for first cycle only in case of multiple cycles) and the double value, in parentheses, the data spread.

	Increasing Pressure			Decreasing Pressure	
	R_I	R_{II}	R_{III}	R_I	R_{II}
Single crystal	1.470 (1.280-1.890)	0.191 (0.160-0.254)	0.559 (0.430-0.650)	1.560 (1.31-1.940)	0.199 (0.134-0.254)
Polycrystal	1.455 (1.340-1.570)	0.204 (0.180-0.230)	0.548 (0.507-0.570)	1.520 (1.390-1.720)	0.204 (0.180-0.210)
Bridgman[1]	1.514	0.239	0.616	—	—

As can be noted, the average values of the relative resistance for the three phases at the point of transition upon increasing pressure are similar to those reported by Bridgman for single crystals. Since the single crystals in this program were of random orientation, the values vary considerably, which simply reflects anisotropy in the resistivity and pressure coefficient of resistivity. As would be expected due to its randomizing effect on anisotropy, the data spread for the polycrystalline specimens is somewhat smaller than that observed for the single crystals.

There is a difference, again being larger in the case of the single crystals, between the relative resistance of Phase I and II observed under increasing and decreasing pressure. Bridgman[1] also observed a similar effect and mentioned that it might be associated with a change from a single to polycrystalline structure as a result of passing through the I-II transition, thus reducing, or eliminating, the anisotropy inherent in the original single crystals. As will subsequently be shown, the original single-crystalline structure is lost as a result of passing through the I-II transition, which could account for such an observed difference. However, even in the case of the original polycrystalline samples where one naturally assumes complete, or near complete, isotropy, there is a marked difference between the relative resistance at the point of transition, particularly of phase I, for increasing and decreasing pressure. This, along with the fact that the final resistance differs from the original, indicates that the polycrystalline structure formed as a result of passing through the II-I transition may exhibit substantial orientational regularity ("texturing"), thus differing from the initial isotropic polycrystalline structure. This residual polycrystalline structure common to all initial structural conditions will be subsequently discussed.

C) Transformation Rate. The transformation rate associated with subject transition varies widely from test to test and within any given pressure run. For example, whereas in Fig. 3 the single-crystal sample transforms more rapidly in the case of the I-II transition, in other experiments the polycrystal transforms at a higher rate. There appears, however, to be no reproducible effect of initial structure upon the transformation rate or any indication that one of the transitions was more sluggish than the other.

As would be expected, the rate of transformation is highly dependent upon the pressurization rate. At the higher rates, the transitions often initiate while pressure is being changed, in which case it proceeds rapidly, reaching completion in as little as 10 sec. At the slower pressurization rates (Fig. 3 being a typical example of the 100-atm increment procedure), the transition may require several minutes to go to completion.

If one assumes that relative resistance change is proportional to the volume percentage of the two phases present at any given time, then the curves, shown in Fig. 3, are similar in shape to that predicted based on nucleation and growth theory for an isothermal transformation.[6] It is indicated, therefore, that the pressure-induced I-II and II-III transitions in bismuth are thermally activated nucleation and growth-type processes in contrast to the very rapid nonthermally activated diffusionless type (often called martensitic) as observed in such pure metals as lithium, cobalt, and zirconium.

D) Microstructural Analysis. Typical residual structures for single and polycrystalline bismuth after cycling through the I-II transition are shown in Figs. 5 and 6 and for I-II and II-III transitions in